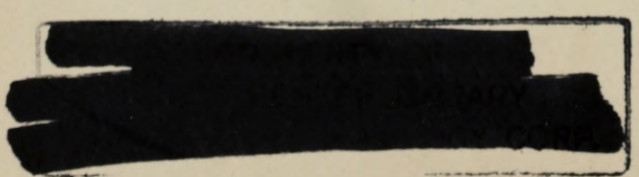
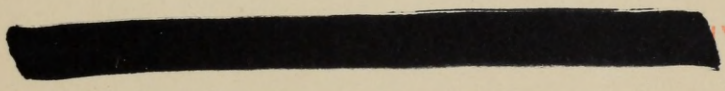
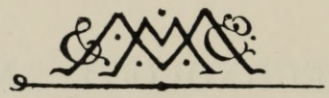




CHEMICAL TECHNOLOGY AND ANALYSIS

OF

OILS, FATS, AND WAXES



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CHEMICAL TECHNOLOGY AND ANALYSIS OF OILS, FATS, AND WAXES

BY

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CONSULTING AND ANALYTICAL CHEMIST, AND CHEMICAL ENGINEER EXAMINER IN "SOAP MANUFACTURE" AND IN "FATS AND OILS" TO THE CITY AND GUILDS OF LONDON INSTITUTE

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ERRATA AND ADDENDA

Page 49, line 8 from bottom, *for* Cowper-Hewitt *read* Cooper-Hewitt.

,, 60 ,, 12 ,, *for* vernica *read* vernicea.

,, 60 ,, 12 ,, *add after* Corr. : *Dryandra cordata*, Thunb.

,, 122 ,, 12 from top, *for* (téon) *read* (téou).

,, 274 ,, 2 from bottom, *for* europea *read* europæa.

,, 314 ,, 14 ,, *for* mauritania *read* mauritiana.

,, 425 ,, 3 from top, *for* Zaha *read* Za.

,, 425 ,, 4 ,, *for* grandidieri *read* Grandidieri.

,, 431 ,, 13 from bottom, *for* Siack *read* Siak.

,, 491 ,, 15 ,, *for* rosin *read* resin.

,, 492, delete line below footnote 1, and cp. Appendix, p. 492.

,, 535, line 6 from bottom, *for* callophylla *read* calophylla.

CHAPTER XIII

COMMERCIAL PREPARATION OF THE RAW MATERIALS USED IN THE OILS, FATS, AND WAXES INDUSTRIES

Commercial Preparation of Oils and Fats

Oils and fats serve the human race as one of the most important articles of food. Hence operations having for their object the preparation of oils and fats date back to the remotest times in the history of mankind. The cave-dweller who first collected the fat dripping from the deer on the roasting-spit may be considered as the first manufacturer of tallow, just as the inhabitant of a tropical country who first collected the oil which ran off the broken kernel of the cocoa nut, on exposure to the sun, may be looked upon as the first manufacturer of vegetable oils or fats. The technical appliances used for the production of oils and fats therefore range from the simplest contrivances up to the very elaborate machinery in vogue at present. Some of the oldest appliances still survive to-day, such as the extremely primitive methods employed in the production of palm oil, the expression of olives, the boiling out of blubber, etc. The first supplies of vegetable oils and fats were, no doubt, obtained from fruits, such as those of the palm and olive trees. The oils were recovered in an exceedingly crude fashion, either by storing the fruits for some time in holes in the ground, when fermentation of the mass set in and the oil rose to the surface, or by boiling the fruit in water.

An advance in the manufacture was reached with the expression of oils from fruits in some kind of a rough press, exemplified by packing the fruit into sacks, and covering these with boards weighted by stones. A further stage was marked by the production of vegetable oils from oleaginous seeds; these were originally ground up between stones, as is still being done at present in East India. The latest development is indicated by the processes involving the extraction with solvents.

Since oils and fats are obtainable in all countries of the world, it will be readily understood that even the crudest and oldest methods are still in existence. The detailed consideration of these modes of manufacture lies beyond the scope of this chapter, and the reader

must be referred to the following chapter, in which, under the heading of each individual oil or fat, manufacturing processes are described. Nor is it intended to give an exhaustive survey of the subject and to describe in detail the more recent manufacturing operations. We shall therefore only briefly glance at the stages by which the most advanced technical processes and appliances used in large scale operations have been reached.

The processes employed for the production of **oils and fats** divide themselves naturally into three classes :—

(1) Preparation of oils and fats by rendering, *i.e.* boiling out with water or steam.
(2) Preparation of oils and fats by expression.
(3) Preparation of oils and fats with the aid of solvents.

(1) *Preparation of Oils and Fats by Rendering, i.e. Boiling out with Water*

A survival of the oldest methods of rendering *vegetable oils and fats* (still practised in Central Africa, Indo-China, and some of the South Sea Islands) by heaping up oleaginous fruits and allowing the contained oil to melt by the heat of the sun and run off to be collected (see Chap. XIV. "Carapa Oil," "Caÿ Caÿ Fat"), is at present represented by the system of preparing Cochin oil (see Chap. XIV.) by boiling out the sun-dried or kiln-dried cocoa nuts with water.

Since the simplest machinery is required for a process of this kind, the method has still some fascination for inventors, and even at the present day processes are being patented having for their object the boiling out of fruits with water or salt solutions,[1] so as to facilitate the separation of the oil from the pulp by gravitation. Processes of this kind have been patented by *Graham* and *Kellogg* (German patent 109,239), *W. H. Gesner* and *A. R. Brandly* (French patent 357,329), and by *Miguel del Prado*, Lisbon (French patent 365,187) (cp. also *Tanquerel*, French patent 345,849, Chap. XIV. "Olive Oil"). Whereas the boiling-out process is of minor importance in the preparation of vegetable oils and fats (except Cochin oil), "rendering" is applied on the largest scale to the production of *animal oils and fats.* Formerly animal oils and fats were obtained by heating those parts of the animal which contained oil or fat, so as to cause bursting of the fat-containing cells. Not infrequently the tissue would burn on to the sides of the vessel and lead to the destruction of the fat, or the fat would even boil over and run into the flue, whereby volumes of acrolein were sent into the atmosphere.

This rough-and-ready method of heating the adipose tissue of the animals over free fire may be considered as extinct in properly

[1] The heating of fat-containing material with an oil or fat similar to that which it contained has been patented by Berliner (English patent, 23,146, 1907 ; United States patent, 878,930 ; German patent, 197,725 ; French patent, 383,231).

equipped establishments, but it is still being practised in small works on the Continent. The nuisance which follows in the wake of a manufacturing process of this kind has naturally led to stringent regulations on the part of the sanitary authorities.

Even the practice of "trying," *i.e.* rendering, the blubber of the whale, seal, and sperm whale (see below) on board the whaling vessel over free fire has become obsolete, and the modern practice is to deliver the blubber in as fresh a state as possible to the whaling establishments, where the oil is rendered in digesters (see below, Chap. XIV. "Whale Oil," "Seal Oil").

The rendering of tallow from the "rough fat" as it comes from the slaughter-house to the rendering establishment is nowadays carried out under such conditions that no serious objections can be raised from a sanitary point of view. The simplest, and, as I can testify from my own experience, a very effective method for obtaining tallow for technical purposes, is to throw the rough fat into covered lead-lined vessels provided with steam coils, outlet taps, a trap-door for charging the rough fat, and a wide outlet through which any offensive vapours that may be given off are conducted through closed pipes to the chimney stack or fire grate.[1] Hot water is then run on to the fat, and steam turned on. After heating for a sufficient length of time, the steam is shut off, when the clear melted fat rises to the top. It can then be drawn off ready for use or into another vessel for further purification (see below, "Refining," "Bleaching"). The animal tissue, etc., still containing considerable quantities of fat, is boiled up again with steam after a few per cent of dilute sulphuric acid have been added, whereby the cell membranes are "cut," so that they more readily part with the remainder of the occluded fat.

This second operation yields a somewhat inferior kind of fat as regards odour and colour; the proportion of free fatty acids is, however, not increased thereby, since dilute sulphuric acid is incapable of effecting hydrolysis.[2]

The foregoing method yields, for technical purposes, good raw material. Therefore processes (patented recently) involving the melting out of rough fat *in vacuo* are an unnecessary complication of a simple operation.

Since melting the rough fat over free fire has been classed amongst the noxious trades, a number of apparatus have been designed in which the tallow is melted in closed vessels under pressure. Such vessels—termed digesters—consist essentially of a vertical boiler provided with a false perforated bottom, and constructed to withstand a pressure of several atmospheres. Live steam is turned into the boiler below the perforated bottom on which the rough fat rests; at the elevated temperature the mass parts readily with its occluded fat, and in a shorter time than by steaming at the ordinary pressure. An apparatus of this kind, designed by *Wilson*, is shown in Fig. 1;

[1] Cp. French patent, 382,745 (G. Talbot).

[2] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1903, p. 73; also Vol. I. Chap. II.

it has served as a prototype for a number of more or less complicated digesters now in use.

The rendering of lard in the large packing houses in the United States is carried out on similar lines. More primitive are the methods for obtaining fish, blubber, and liver oils. These methods, as also the rendering of animal oils and fats for edible purposes, will be described under the headings of the individual oils and fats in the following chapter, and in Vol. III. Chap. XV.

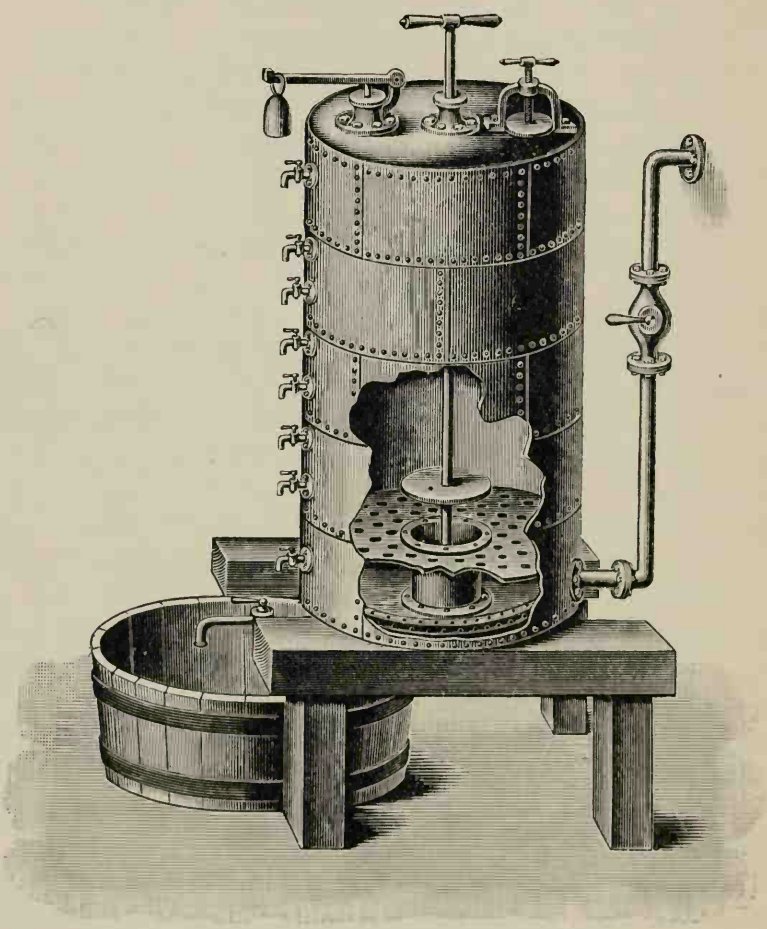

Fig. 1.

The employment of digesters has found most extensive use in the enormous rendering establishments for tallow, bone fat, and lard, in the United States and South America (see Chap. XIV.), which in their turn have served as models for the rendering of blubber oils (see Chap. XIV. "Whale Oil"), fish oils (see Chap. XIV.), bone fat (see Vol. III. Chap. XV.), "Greases" (see Chap. XV. and Chap. XVI.), and all kinds of waste fats in slaughter-houses (see Chap. XVI.). Side by side with the processes using digesters, there are still in vogue, on a large scale, processes having for their object the boiling out of oil-containing material with the aid of water and steam in open vessels (see Chap. XIV. "Fish Oil," "Neat's Foot Oil").

The preparation of animal oils and fats for edible purposes requires special precautions, which vary with the special conditions which each individual material presents. A description of some of these processes will be found in Chapter XIV., under the headings "Lard," "Tallow," "Butter," "Cod Liver Oil," and in Volume III., under the heading "Margarine."

(2) *The Preparation of Oils and Fats by Expression*

The boiling-out process is, of course, practically inapplicable in the case of small seeds such as linseed and rape seed. The original method of obtaining the oil from such seed has most likely been the same which is still used in India, viz. trituration of the seed in a mortar, so that the oil can exude. It may be safely assumed that the process of expression was applied in the first instance to the preparation of olive oil. The first woman who expressed olives by packing them in a sack and weighting with stones may be considered the forerunner of the inventors of all the presses that subsequently came into use. Pliny describes already in detail the apparatus and processes employed for obtaining olive oil amongst his Roman contemporaries, who used a simple screw press, a knowledge of which they had derived from the Greeks. In the East, where vegetable oils not only form an important article of food, but are also used for other domestic purposes, various ingenious applications of lever presses and wedge presses, and even of combined lever and wedge presses, have been employed from the remotest times. At an early stage of history the Chinese employed the same series of operations which are followed in the most advanced oil mills of modern times, viz. bruising and reducing the seeds to meal under an edge stone, heating the meal in an open pan, and pressing out the oil in a wedge press, in which the wedges are driven home by hammers. This primitive process is still being carried out in the production of the soja bean cake and soja bean oil (see Chap. XIV. "Soja Bean Oil"), one of the staple industries of Manchuria. The remarkably good yields of oil which are thus obtained must be due to the length of time the meal is kept under pressure. The Japanese employed similar methods, and at the present time a special wooden wedge press—*tatsugi*—is largely employed in the oil industry of Japan. The olive press, which was also used in vineyards for expressing the grape juice, found its way from the South of France to the North, and was commonly employed for the expression of poppy, hemp, and rape seeds. The apparatus was then gradually improved, and thus were evolved the modern forms of the screw press, next the Dutch or stamper press, and finally the hydraulic press.

With the screw press, even in its most improved form, the amount of pressure practically obtainable is limited owing to the failure of its parts under the severe inelastic strain. Hence this form of press finds only limited application, as in the olive oil industry, for expressing the best and finest virgin oil, and in the production

of animal fats for edible purposes, such as lard and oleo-margarine.

The Dutch or stamper press, invented in Holland in the seventeenth century, was up to the early years of the nineteenth century almost exclusively employed in Europe for pressing oil seeds. This press consists of two principal parts, an oblong rectangular box, with an arrangement of plates, blocks, and wedges, and over it a framework with heavy stampers which produce the pressure by their fall. The press box first consisted of strongly bound oaken planks, but later on cast-iron boxes were introduced. At each extremity of the box, a bag of oil meal was placed between two perforated iron plates, under which were a perforated bottom and channels for conducting away the expressed oil. Next were inserted filling-up pieces of wood, two of which—the speering blocks—were oblique or bevelled on one face, forming ways for the two wedges which pressed against them. Between the speering blocks, and separated also by a filling-in piece, were inserted the two wedges, one being the ordinary or driving wedge by which the pressure was applied to the seed bags, and the other an inverted or spring wedge, which was only driven down to loosen and free the various parts when the pressing operation was completed. The stamper which drove home the ordinary wedge was a heavy log of wood, about 16 feet long by 8 inches square, and it fell about fifteen times a minute through a maximum distance of 22 inches, by the action of a pair of cams fixed on a revolving shaft. When the pressure was deemed to have acted a sufficiently long time, the stamper suspended over the inverted wedge was brought into action ; by a single heavy blow it knocked the wedge out of its key-like position and thus freed the various parts of the apparatus for the removal of the pressed cakes.

This press has had to give way to the hydraulic press, although in some old-fashioned establishments in Holland the stamper press could still be seen at work in the eighties of the last century.

The invention of the hydraulic press in 1795 by *Joseph Bramah* (English patent, 30th April 1795), effected the greatest revolution in the oil industry, introducing as it did a new, easily controlled, and almost unlimited source of power ; the limit of the power being solely reached by the limit of the strength of the material the engineer is able to produce. Since then the hydraulic press has practically completely superseded all other appliances used for expression. In consequence of this epoch-making invention, assisted as it was later on by the accumulator—invented by William George (later Lord) Armstrong (in 1843),—the seed-crushing industry reached a perfection of mechanical detail which soon secured to England the supremacy in this industry, at any rate up to the end of the last century.

The machinery required for the preliminary treatment of the fruit or seed will naturally vary with each particular kind of fruit or seed ; thus the preparatory operations for laying bare the fat-containing cells of cocoa nuts differ entirely from those necessary in the case of linseed.

A description of the special methods used for the expression of each individual oil and fat will be given in the following chapter. Here it must suffice to glance at the modern methods of preparing, crushing, and expressing the oleaginous seeds, as carried out in the best-equipped establishments.

Since the catalogues and advertisements of the engineering firms who make a speciality of this class of machinery supply excellent illustrations, it is not deemed necessary to reproduce them here, it being my intention in this work to lay greater emphasis on the chemical technology and general principles of the industries than on a full description of the machinery[1] used and the details of manufacturing operations.

The storage of the seeds requires special precautions. They must be kept dry so as to prevent heating, especially if they be brought into the store-house in a moist state. The enzymes in the seeds then act on the oil or fat, producing hydrolysis with the formation of mono- and diglycerides and of free fatty acids (this is readily detected in the case of moist rape seed, as under favourable conditions the diërucin formed crystallises out from the oil). The free fatty acids so formed are acted upon by the oxygen of the air, so that on pressing such seeds oils are obtained, which not only contain free fatty acids, but also leave the presses in a rancid state.

The sequence of operations in treating oil seeds, oil nuts, etc., for the separation of their contained oils is at the present time as follows :—As a preliminary operation the oil seeds and nuts are freed from dust, sand, and other impurities, by sifting in an inclined revolving cylinder or sieving machine covered with woven wire, having meshes varying according to the size and nature of the seed operated upon. This preliminary purification is of the greatest importance; it is especially indispensable for the preparation of edible oils and fats. In the case of those seeds which contain pieces of iron (nails; hammer heads in the case of palm kernels), the seeds are passed over magnetic separators, which retain the iron. The seeds and nuts are decorticated (where required), the shells are removed by mechanical means (sifters, blowers), and the kernels ("meats") converted into a pulpy mass or meal by passing through a hopper over rollers, consisting mostly of five chilled iron or steel cylinders, mounted vertically like the bowls of a calender (in older establishments by stamping or crushing and grinding between stones in edge runners). These rollers are finely grooved, so that the seed is cut up whilst passing in succession between the first and second rollers in the series, then between the second and third, and so on to the last, until it is sufficiently bruised, crushed, and ground. The distance between the rollers can be easily regulated so that the seed leaving the bottom roller has the desired fineness.

The suitably comminuted mass, forming a more or less coarse powder ("meal") is either expressed at the ordinary temperature, or

[1] Cp. Lewkowitsch, Cantor Lectures on "Oils and Fats: their Uses and Applications," *Journ. Soc. Arts*, 1904.

subjected to preliminary heating, the latter depending on the quality of the product to be manufactured. For the preparation of edible oils and fats, the mass is packed in bags and expressed in hydraulic presses *in the cold*, under a pressure of 300 atmospheres or more (equalling a pressure of two tons or more to the square inch), so that the oil may exude readily. Such oils and fats are known as *salad oils, cold-drawn oils, cold-pressed oils* (see Vol. III. Chap. XV. "Edible Oils"). Under these conditions the oils and fats dissolve the smallest amount of colouring matters, and suffer in the least degree as regards quality. Obviously only a portion of the oil or fat contained in the fruits or seed is obtained in this manner; a further quantity is gained by expression at a somewhat elevated temperature, which is reached by warming the seed previous to expression. The quality of the oil or fat naturally suffers when expressed in the hot, more of the extractive substances being dissolved in and intermixed with the oil. The taste also suffers; the oil thus obtained is hardly suitable for edible uses and is chiefly employed for manufacturing purposes. The oil or fat which is retained by the press cakes can only be recovered by again comminuting the latter and subjecting the meal so obtained to a further expression.

In the case of oleaginous seeds of somewhat low value, such as linseed, cotton seed, the aim is to express in one operation the largest possible quantity of oil. Hence the broken seed is generally warmed in a steam-jacketed kettle, fitted with mixing gear, by passing steam into the jacket, and sending at the same time some steam through a "rose," fixed inside the kettle, into the mass while it is being agitated. This practice is a survival or rather persistence of the older method of moistening the seed with a little water while the seeds were bruised under an edge runner, so as to lower the temperature, and facilitate the bursting of the cells. The assumption that the albuminous mass is thereby coagulated hardly holds good, the object being merely to warm the seed to a higher temperature and at the same time to moisten it, so that the cells part more freely with the imprisoned oil.

The heated meal is then either packed by hand as is being done largely in the South of France in "scourtins" (bags made of plaited aloe leaves or cocoa nut leaves, camel hair or horse hair), or delivered through a measuring box, which is combined with an automatic moulding machine, into woollen bags or open cloths ("Anglo-American press"), so that the preliminarily pressed cakes can be put at once into the hydraulic press, in which the meal is subjected to high pressure. In the latest modern constructions of cage presses (see below), the use of bags is entirely dispensed with, a measured-out quantity of seed falling direct into the circular press cage, and being separated by a circular plate of sheet-iron from the material which is to form the next cake.

The essentials for proper oil pressing are a slowly accumulating pressure, so that the liberated oil may have time to flow out and escape; a pressure that increases in proportion as the resistance of

the material increases, and that maintains itself as the volume of material decreases through the escape of oil. Numerous forms of hydraulic presses have been devised. The various forms of oil presses may be divided into vertical and horizontal presses. Horizontal presses have practically ceased to be used in this branch of industry. At present vertical presses are almost exclusively in vogue.

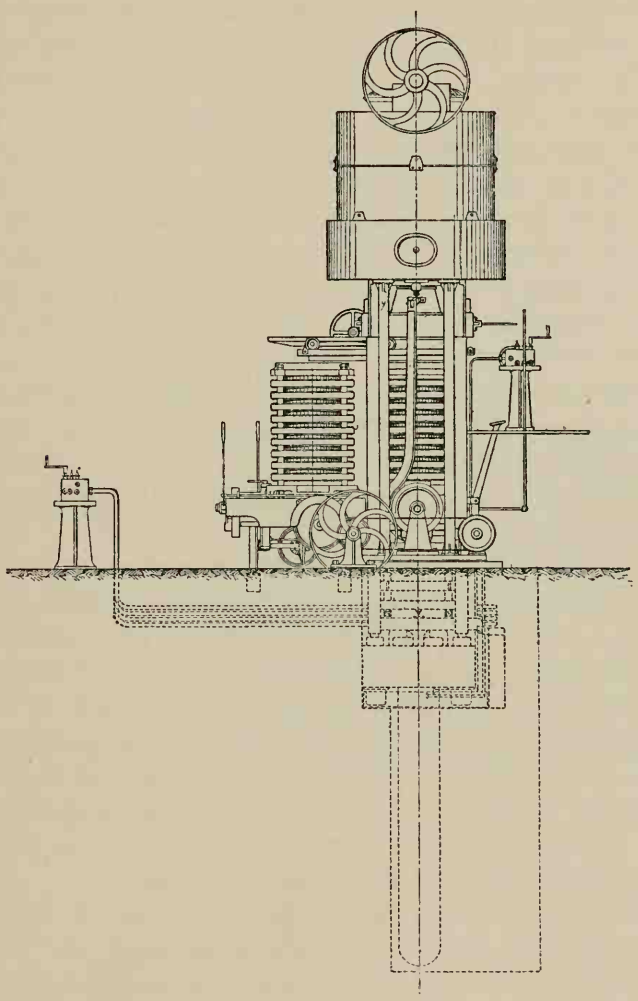

Fig. 2.

The most primitive form of vertical press, and one which is still used where high pressure is not essential, is a drum or a box press, so called because on the platten are placed two circular metal tubes, one within the other, the inner being perforated throughout for the escape of the oil. At the top of the press is secured a strong metal plate or table, having the same diameter as the inner box. When the ram carrying the box is forced up against the surface of this table the seed is pressed. The seed bags, separated by metal plates, are deposited within a perforated box. Experience, however, has demonstrated that the best presses are those provided with separate trays or seed boxes for each bag, and the ordinary oil press of this

type is fitted with 4 to 6 seed boxes, and presses 4 to 6 separate cakes at one working. A convenient form was the double oil press of *Blundell*, which admits of continuous working, one division being under pressure while the other division is being emptied and recharged. This press has been practically ousted from the market by the following three types of presses :—

1. *The Marseilles Press.*—This press, a "pack press," dispenses with bags, seed boxes, and hair mats, the seed being packed by hand in "scourtins," to the number of 16 to 25 for one charge, the "scourtins" being simply separated in the press by corrugated iron plates. This press is still largely used in the South of France, although the packing requires more manual labour than in the case of the Anglo-American press (see No. 2). Moreover, this press offers inconvenience in keeping the bags straight, and the pressure cannot be raised to the same height as can be done in the following two types of presses. In fact, the extreme limit of pressure is 250 to 300 atmospheres (34 to 40 cwts. per square inch), this being the limit of the resistance of the "scourtins."

2. *The Anglo-American Press.*—This vertical press is at present the one mostly in use.[1] It consists of an open press fitted with a number of iron press plates (from 10 to 16) between which the cakes are inserted by hand. The pressure employed with these presses is usually 2 tons per square inch.

3. *Cage Press* (*Clodding Press*).—This is a hydraulic press provided with a circular box or cage, into which the meal is filled as described above. The box (cage) is either constructed of metal staves (see Fig. 4) (vertical steel bars), held together by a number of steel rings, or consists of one cylinder having a large number of perforations. The presses having perforated cylinders, although presenting mechanically a more perfect arrangement, are not preferable to the presses formed by staves, as the holes easily become clogged up by the meal, and it then becomes necessary to clean out the cylinder, an operation which involves a good deal of labour.

In order to save time and to obtain an increase of output with a given number of Marseilles or cage presses, each set (battery) of presses is provided with a preliminary (preparatory) press, in which the meal bags are compressed under a pressure not exceeding 15 to 20 cwts. per square inch. The shrinkage in volume caused by the outflow of oil is made up by bags containing fresh meal.

When the presses are charged the hydraulic pressure from the accumulator, and finally from the hydraulic pump, is allowed to act on the ram. The hydraulic ram then compresses the cakes, whilst the exuding oil flows down the sides, in the case of the open presses (1 and 2), or through the openings between the staves (clodding presses), or through the perforations of the cylinder, as the case may be, into a tank below. After releasing the pressure, the hot cakes

[1] *A. Austerlitz* (French patent 381,350, English patent 10,860, 1907) claims to obviate certain drawbacks to this press.

are taken out; the edges, which are naturally richer in oil than the bulk, and hence are soft and friable, are trimmed off in a paring machine.

Oil obtained from the heated meal is usually more highly coloured and harsher to the taste than cold-drawn oil, since larger quantities of the extractive substances (albuminoids, mucilaginous substances) are dissolved in, and intermixed with, the oil. According to the care exercised by the manufacturer in regulating the range of temperature through which the seed is heated, various grades of oil are obtained.

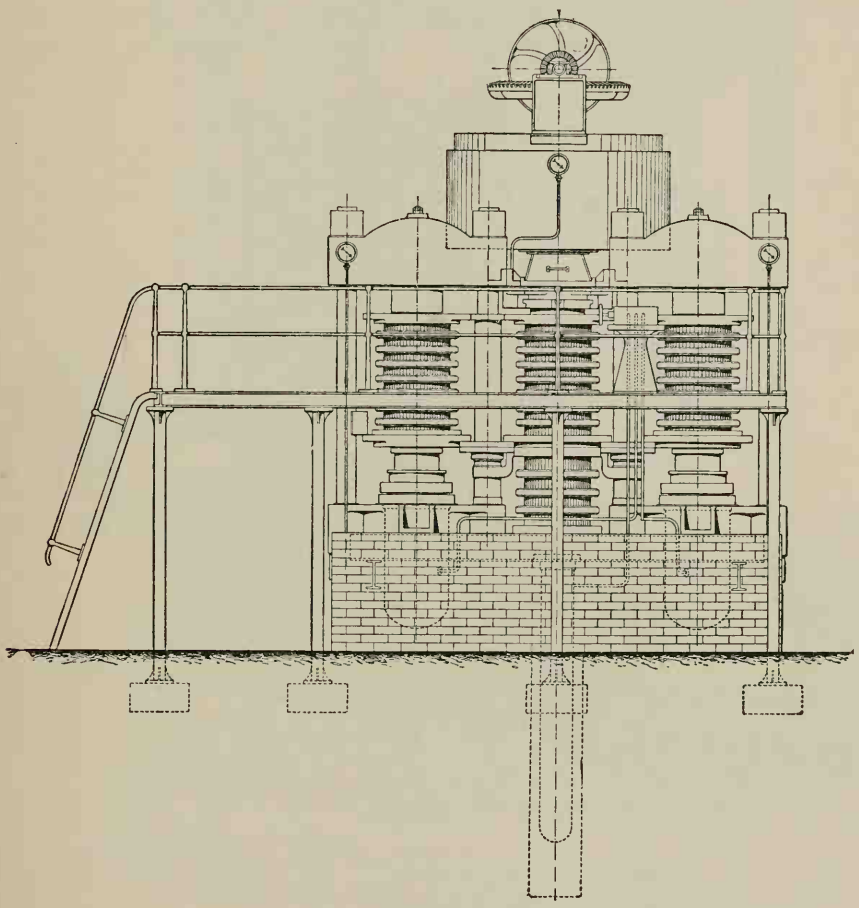

Fig. 3.

When the seeds contain large amounts of oil, exceeding 40 per cent (palm kernels, cocoa nuts, castor seeds), it is necessary to repeat the process of expression. This is done by breaking up the cakes in a cake-breaking machine, reducing them to meal, and subjecting the latter to a second expression in the manner described already.

In the case of some oil seeds which contain more than 40 per cent of oil (arachis, sesamé) the first expression in bags leads to difficulties, as the oily meal causes "spueing," *i.e.* the meal exudes and escapes from the presses.

Hence in modern installations the first expression of these seeds

is carried out in "clodding" presses. These presses, generally worked in sets of two, or three, or more, have a seed kettle fixed on the top of the press (see Figs. 2 and 3); the kettle is provided with one or more openings, corresponding to the chamber or chambers in the heads of the press or presses. These chambers can be closed at the top and bottom by slides, actuated by levers, and are designed to contain as much meal as is required to form one cake. The measured charge of meal is then allowed to fall into the press box and is covered with a circular metal plate. This operation is repeated until the press is full, when hydraulic pressure is applied, and a ram forces the box against a sliding block at the head of the press. The oil exudes, and the meal is pressed into circular cakes ready for the

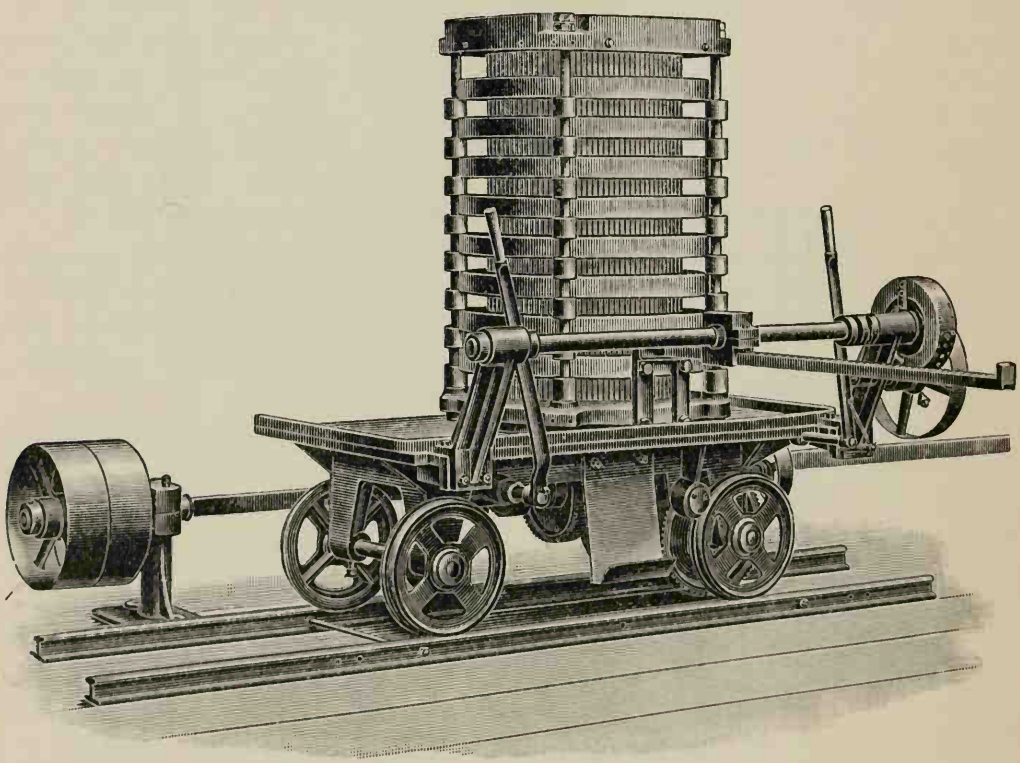

Fig. 4.

second expression. After releasing the pressure, and removing the sliding block, the cakes are forced out by the hydraulic ram. They are then broken into meal and subjected to a second expression in a Marseilles or Anglo-American hydraulic press.

The mechanical part of the process has been improved recently, so that even for the second expression the open Anglo-American press can be dispensed with. The finishing presses are made of the same type as the press in which the first expression is carried out, and by making the press cages removable, the pressing operation may become an almost continuous one. These cages can be transported by means of a power-driven carriage (see Fig. 4) to the finishing presses, or where one preliminary press is combined with two finishing presses to a battery, the cages can be conveyed into the adjoining

finishing press by a swinging arrangement (see Figs. 5 and 6), their place being filled immediately by a charged cage, or by a cage containing finished cakes. Thus, with the exception of the time required for withdrawing the pressing cages and replacing them, the work

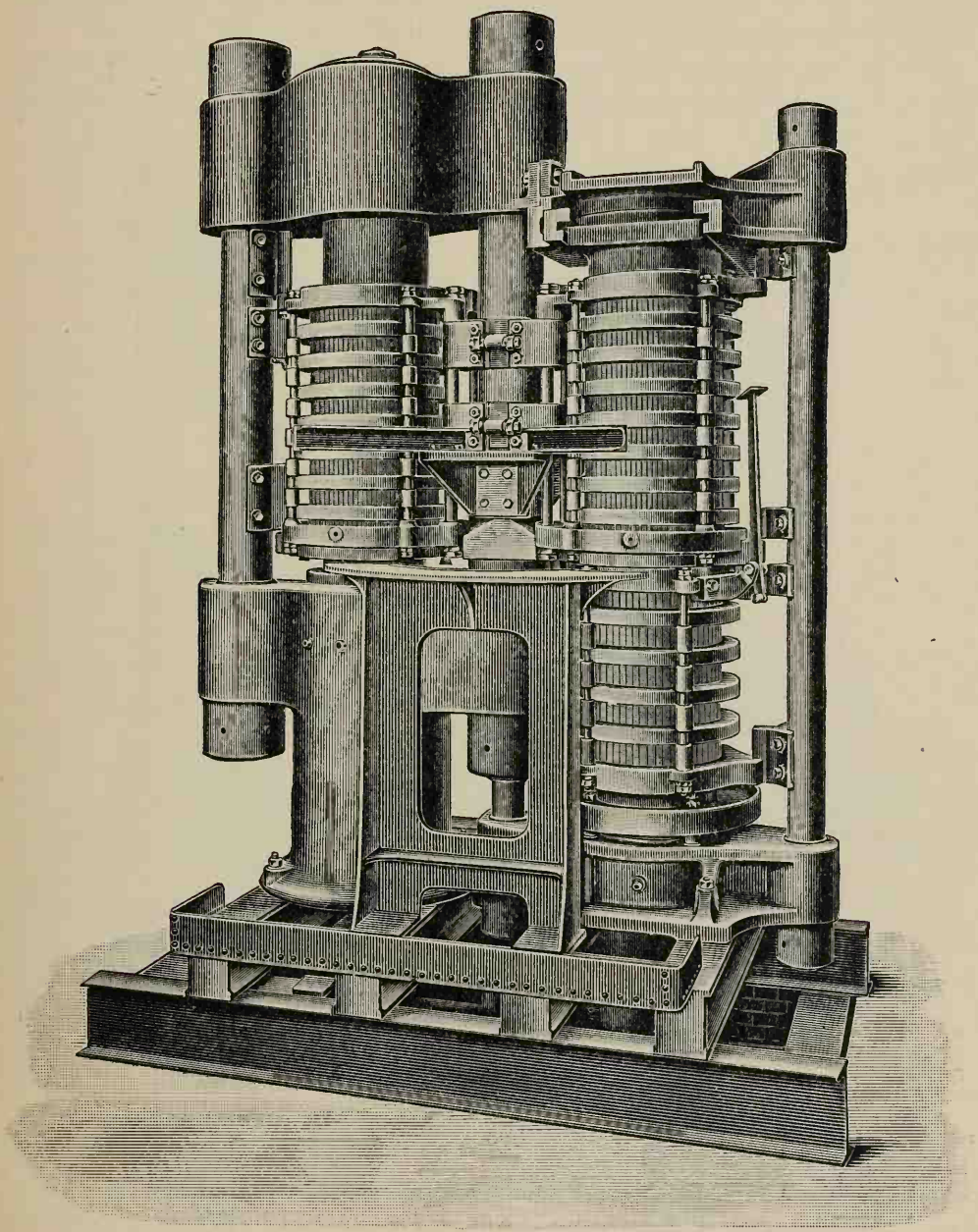

Fig. 5.[1]

goes on practically continuously. Further advantages are offered by these presses in that the cakes require no paring, and that a saving of "scourtins" or press cloths in comparison with the Marseilles or Anglo-American systems is effected.

[1] The illustrations Figs. 2-6 have been engraved from drawings and photographs kindly lent by Messrs. Greenwood and Batley, Leeds.

In the cage presses a higher pressure can be employed and hence more oil can be obtained from the meal than in the open types (the Marseilles and Anglo-American presses). The pressure can be run up in practice from $2\frac{1}{2}$ to $2\frac{3}{4}$ tons per square inch. If the open presses could be made to withstand the same high pressure, they would undoubtedly yield the same amount of oil.

The cage presses having perforated cylinders (see above) are designed for still higher pressures, and installations have been erected

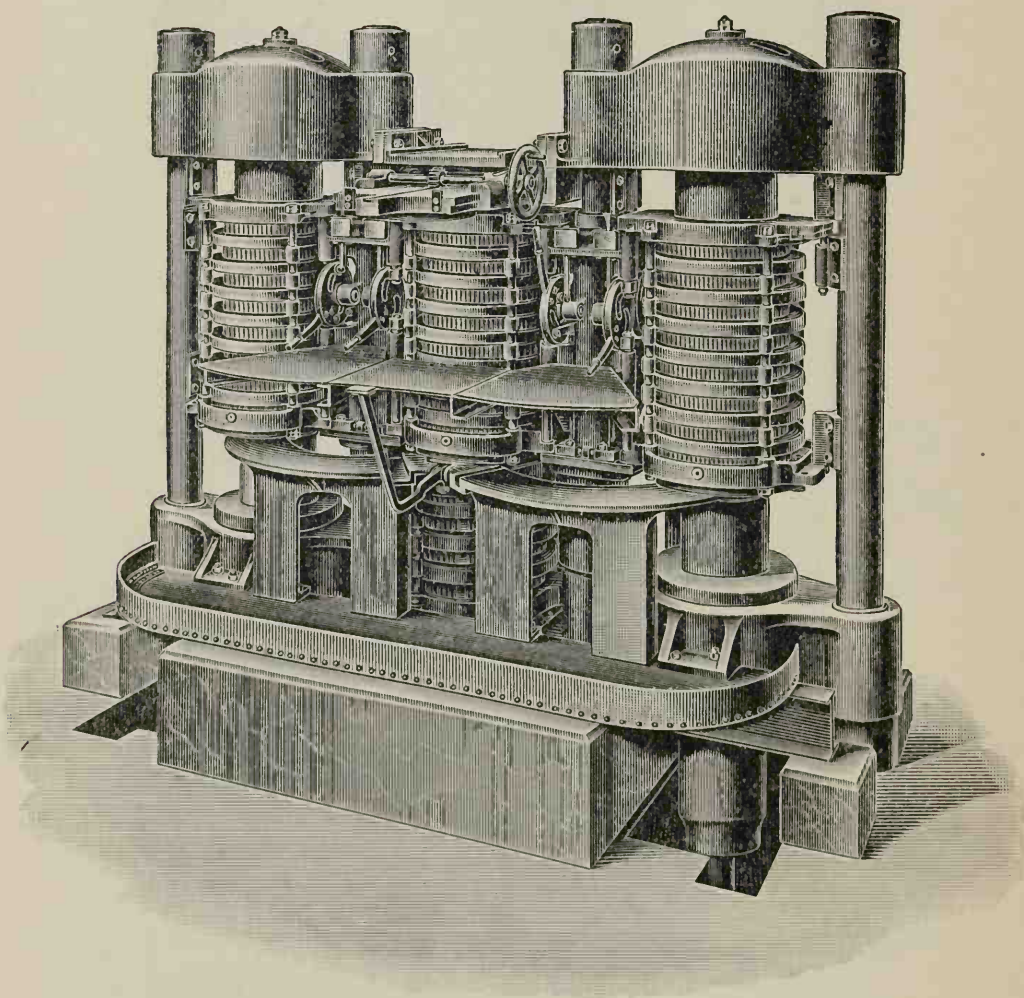

Fig. 6.

during recent years in which the pressure (under the piston) amounts to 450 atmospheres (3 tons per square inch), and even 600 atmospheres (4 tons per square inch). In order to provide for a ready outflow of the oil the number of holes in a cylinder of 420 millimetres diameter and 1400 millimetres height has been increased to almost 60,000. It should, however, be pointed out that no advantage is gained over the open presses or cage presses fitted with staves by these very high pressures. True, the cakes retain only about 7 per cent of oil, but stock-raisers prefer cakes containing 10 per cent of oil (excepting cakes made from undecorticated cotton seed).

In addition to the drawback mentioned already, the high prime cost of installing these expensive presses must militate against them. It has been ascertained in practice that the working expenses and the yield of oil of equal quality are almost identical in installations of the older types and in mills having the cage presses working under these extremely high pressures, whilst the initial outlay for these latter presses is from three to four times higher. Moreover, the oil produced under the higher pressure is more turbid than oil obtained in the older types of presses, and is more difficult to clarify. This is no doubt due to a larger amount of extractive substances having passed into the oil.

Therefore the alleged advantages claimed for these presses have not been borne out, so far, in practice.

It should be noted that the above figures given for the pressures represent the pressures under the press piston, as read off the manometer. They by no means indicate the pressures on the cakes themselves. As a general rule it may be accepted that the cakes are under a pressure of about two-thirds of that indicated by the manometer.

The oil flowing down the sides of the press or through the staves or holes is caught in reservoirs placed below the level of the floor and is pumped into store tanks for settling, clarifying, and refining (see below).

Although the modern presses described above work economically, still there adheres to them the obvious drawback that the work is not an entirely continuous one. This feature has induced, at an early period, several inventors to design continuously working presses, such as those of *Bessemer* and *Haywood* (English patent 1261, 1849), *Müller* (German patents 26,343, 1883; and 35,781, 1889), *Bergreen* (German patent 65,165, 1892). But not one of these presses has been able to maintain itself in practice owing to the high cost required for power, in conjunction with a very small throughput. Recently experiments have been made in several European oil mills with an automatic press, designed by *V. D. Anderson.* In this press the seeds are introduced through a hopper and carried forward by screw blades into a horizontal cage formed by metal staves. The spirally arranged blades do not set the mass in rotation, but subject the seeds to a force of torsion by contact with the mass in front of them. The expressed seed is driven on to the end of the horizontal cage, and as soon as a certain pressure is exceeded a portion of the expressed mass is discharged.

This press works on cold seed only, and therefore the oil which is obtained is of very good quality.[1] The press is especially recommended by the inventor for linseed, rape seed, and cotton seed. His claim that only 5 per cent of oil are left in the ejected mass has, however, not been borne out by experiments with which the author is acquainted. Thus, in the case of cotton seed, the pressed material

[1] Cold-pressed linseed cake is liable to evolve prussic acid (see "Linseed Oil," Chap. XIV.), hence cold-pressed cake must not be fed to cattle.

still contained 7 per cent of oil, although the pressure amounted to 5 tons per square inch, whereas the same material pressed in a hot press of the Anglo-American type yielded cakes retaining 4 per cent of oil only. The comparatively small output, the high cost for power, and the strongly corroding action which the compressed mass exerts on the metal constitute such serious drawbacks that it is very unlikely that this press will displace the above described hydraulic presses.

A press similar in design to the press constructed by *Bergreen*, in that it exhibits the same conical shape of the press chamber and the same general arrangement, has been patented recently by *F. C. Caldwell* (English patent 8696, 1905).

The press differs, however, from *Bergreen's* in that the screw blades, which in the latter's press are arranged spirally on a vertical shaft, are replaced by spiral corrugations, or screw threads, which extend approximately half-way around the solid vertical roller, whilst at the lower end the corrugations extend entirely around the roller. The walls of the pressure chamber are formed by staves (as in cage presses) permitting the passage of oil. The author has had no practical experience with this press, which is stated by the inventor to be particularly applicable to cotton seed and linseed.

V. J. Lauermann (United States America, 876,363) claims an apparatus for the extraction of cotton seed and other oil seeds, consisting of a vertical jacketed cylinder, inside which a shaft provided with arms rotates. These arms are fitted with knives which run parallel to the shaft, and almost touch the wall of the cylinder. There are also fixed knives inside the cylinder. The seed is crushed on passing through the cylinder.

Under this head may also be mentioned the attempts that have been made to use hydro-extractors in the ordinary routine of oil mill work. They are, however, entirely unsuitable for this purpose. Recently, experiments have been made both in Algiers [1] and California [2] to extract, in the first instance, an edible oil from freshly gathered olives by centrifuging the fruit. Nothing definite can, however, be stated as to the advantages alleged to have been obtained, and the reader must therefore be referred to the original publications mentioned in the footnotes.

Hydro-extractors can only be employed with advantage for subsidiary operations in the oil and fat industries, such as for separating the oil from the meal which has exuded through the cloth, or generally from by-products rich in oil.

For the application of centrifugals to the recovery of fat from milk, see "Butter Fat."

The analytical control of this technical process confines itself chiefly to the determination of the proportion of oil or fat contained

[1] Cp. L. Dugast, *L'Industrie Oléicole*, Paris, 1905, p. 78.

[2] *California Olive Oil; its Manufacture.* By G. W. Shaw, College of Agric., Agr. Expt. Station, Bull. No. 158, Sacramento, p. 26.

in the raw material—oleaginous seeds—and the determination of the oil left in the expressed cakes. For these estimations, quantities of not less than 100 grms. should be used.

The sample is prepared for analysis by disintegrating it carefully in a suitable manner, say by means of a cake-mill or coffee-grinder,[1] and exhausting it with ether, or petroleum ether, or carbon tetrachloride,[2] using any of the extracting apparatus described (Vol. I. Chap. IV.). The disintegration of the seeds requires great care, as otherwise considerable quantities of oil or fat may remain in the meal. The breaking up of the cells which occlude the oil or fat is best assisted by grinding with ignited sand, which offers the double advantage of breaking the cells more completely than is done by mere pounding in a mortar, and of presenting a large surface to the extracting solvent. In the case of seeds containing large quantities of oils and fats, it is advisable first to break up the mass roughly and to extract a portion only of the oil or fat, then to triturate the partially extracted mass with sand and finally exhaust completely. This specially applies to copra, palm kernels, and generally to all seeds containing more than 50 per cent of oil or fat.

If ether, or carbon bisulphide, or chloroform is employed, it is necessary to dry the material prior to extraction, moist seeds or cakes being apt to yield up to the solvent non-fatty substances. Ether must first be purified; this is best done by washing with water, in order to remove any alcohol, then drying over calcium chloride, and distilling off; finally the ether is distilled over metallic sodium, in order to free it from the last traces of water and alcohol.

The drying of seeds or cakes containing drying oils, such as linseed and linseed cake, requires some care; if the material has been dried at too high a temperature, or for too long a period, the drying oils refuse to pass readily into solution. This fact is clearly brought out by some experiments recorded in the following table due to *Klopsch*:[3]—

Linseed Cake.	Oil. Per cent.
Dried 3 hours at 94°-96° C. gave . .	8·97
Dried 6 hours at 100° C. gave . . .	8·55
Dried 12 hours at 94°-96° C. gave . .	7·89

If the cakes have been dried at too high a temperature, brown resinous extracts are obtained. An analysis can therefore only be looked upon as correct if the extract has the appearance of a fresh, clear oil.

If petroleum ether or carbon tetrachloride be used as a solvent, the drying of the material may be omitted. The petroleum ether must boil completely below 80° C. This solvent is specially suitable for cakes containing drying oils; moreover, it extracts much smaller quantities of non-fatty substances than ether does.

[1] With regard to errors caused by deviating from these directions cp. *Journ. Soc. Chem. Ind.* 1895, 447.

[2] Bilteryst, *Bull. de l'Assoc. Belge*, 1897 (10), 406.

[3] *Zeit. für analyt. Chem.* 1888, 452.

In special cases the examination of the extracted oil is required. The microscopical examination of the meal will frequently afford assistance.

A large number of analyses of seeds and oil cakes have been published by various observers.[1] These naturally fall outside the scope of this work. I will therefore quote only some analyses by *Nördlinger*[2] as throwing light on the proportion of neutral oil to free fatty acids.

Seeds	100 parts contain		Free Fatty Acids in Total Fat.
	Free Fatty Acids.	Total Fat.	
			Per cent.
Rape (*Brassica rapa*) . . .	0·42	37·75	1·10
Cabbage (*Brassica campestris*) . .	0·32	41·22	0·77
Poppy (*Papaver somniferum*) . .	3·20	46·90	6·66
Earthnut (*Arachis hypogæa*)—			
(*a*) Seed	1·91	46·09	4·15
(*b*) Husks	1·91	4·43	43·10
Sesamé (*Sesamum orientale*) . .	2·21	51·59	4·59
Castor (*Ricinus communis*) . .	1·21	46·32	2·52
Palm nut (*Elæis guineensis*) with 6 per cent husks	4·19	49·16	8·53
Copra (*Cocos nucifera*) . . .	2·93	67·40	4·42

Cakes.	Number of Samples.	100 parts contain		Free Fatty Acids in Total Fat.
		Free Fatty Acids.	Total Fat.	
				Per cent.
Rape . . .	6	0·93	8·81	10·55
Poppy seed . .	10	5·66	9·63	58·89
Earthnut (Arachis)	20	1·42	7·65	18·62
Sesamé . .	15	6·15	15·44	40·29
Palm nut . .	38	1·47	10·39	14·28
Cocoa nut . .	5	1·31	13·11	10·51
Linseed . .	2	0·75	8·81	9·75
Castor . .	10	1·27	6·53	20·07

The total fat was obtained by extraction with petroleum ether, and the free fatty acids were titrated with alkali and calculated to oleic acid.

The ratio of total fat to fatty acids is not necessarily the same in the cakes as in the expressed oils. Thus the "first expressed" oils ("salad oils") contain far less free fatty acids than the total fat in the seeds. Consequently more free fatty acids remain in the cakes. The oils from the second and third pressings are richer in free fatty acids, but still a large portion thereof remains behind in the cakes.

[1] Cp. König, *Die menschlichen Nahrungs- und Genussmittel.*

[2] *Journ. Soc. Chem. Ind.* 1890, 422.

The following example will illustrate this :—

100 Kg. of Poppy Seed yielded	Oil. Per cent.	Containing Free Fatty Acids. Per cent.
When extracted with solvents .	46·9	6·82
When expressed—(*a*) Salad oil .	39·0	1·92
(*b*) Commercial oil	2·5	15·37
There remained in the cakes . .	5·4	38·32

The occurrence of free fatty acids in cakes must also be ascribed to the action of enzymes on the oil retained in the cakes ; and those conditions which favour this action, such as a somewhat elevated temperature (between 30° and 40° C.), moisture, etc., will in stored cakes lead to so notable an amount of free fatty acids, that the cakes become unfit for feeding purposes. Nor must the action of light be ignored. This is clearly brought out by the examination made by *Emmerling*[1] of palm kernel cakes. The following changes were ascertained :—

	Free Fatty Acids in 100 parts of Fat.		
	I.	II.	III.
Fresh cakes	14·35	16·14	20·50
Cakes stored two years in the dark . .	26·44	40·61	...
,, ,, ,, light . .	...	...	86·08

Moulds are another source of the production of free fatty acids in cakes, as they readily grow on cakes stored in a damp condition. In the case of cakes containing drying oils, such as linseed cake, a slow oxidation of the unsaturated fatty acids takes place, leading to the formation of oxidised acids. Such cakes are known in the trade as cakes that have "heated" in storage or during a voyage.

(3) *Extraction of Oils and Fats by Means of Volatile Solvents*

The cakes obtained in the foregoing process still contain considerable proportions of oil, usually 10 per cent, and in the case of undecorticated cotton seed cake 4-5 per cent. If it be desired to obtain larger quantities of oils and fats than can be produced by pressure, processes having for their object the extraction of the seeds by means of volatile solvents must be resorted to.

The solvents employed on a large scale were up to recently almost exclusively carbon bisulphide and petroleum ether. Both solvents suffer from the disadvantage of being readily inflammable.

Extraction of seeds by volatile solvents was first introduced in 1843, by *Jesse Fisher* of Birmingham, who manufactured **carbon bisulphide** on a commercial scale. *Fisher* does not appear to have

[1] *Land. Versuchs-Stat.* 1898, 56.

patented this process. Thirteen years later *E. Deiss* of Brunswick patented (English patent 390, 1856) the extraction of seeds by means of carbon bisulphide, and added "chloroform, ether, essences, benzine, and benzole" to the list of solvents. For several years afterwards this process made little advance, for the colour of the oils produced was high, and the taste was sharp. The extracted oil retained sulphur, which showed itself disagreeably in the smell of the soaps made from it and in the blackening of substances with which it was used. The meal left by the process was so tainted with carbon bisulphide, that it was absolutely impossible to use the extracted meal as cattle food. With the improvement in the manufacture of carbon bisulphide these drawbacks have been surmounted to a great extent, and the employment of carbon bisulphide has specially gained much extension in the extraction of expressed olive marc in the south of France, Italy, Spain, and Tunis. But even now traces of carbon bisulphide are retained by the extracted mass, so that it is impossible to feed cattle with it. Carbon bisulphide is comparatively cheap; cheaper than the commercial benzine used for extracting fat. Being heavier than water, it offers certain advantages in the storage of so volatile and inflammable a liquid, as the vapours can be readily prevented from coming in contact with an open flame. Owing to the physiological effect this solvent has on the workmen, and in consequence of the chemical action of impure carbon bisulphide on iron, which has frequently led to conflagration, the employment of carbon bisulphide must remain restricted.

Petroleum ether was first introduced as a solvent by *Richardson, Lundy*, and *Irvine*, who obtained in 1863 a patent (English patent 2315) for extracting oil from crushed seeds or from refuse cake by the solvent action of volatile hydrocarbons from "petroleum, earth oils, asphaltum oil, coal oil, or shale oil, such hydrocarbons being required to be volatile under 212° F." Since that time the development of the petroleum industry in all parts of the world, and the large quantities of low-boiling hydrocarbons—naphtha—obtained from the petroleum fields, as also improvements in the apparatus originally employed, have raised this system of extraction to the rank of a competing practical method of oil production. The commercial variety of oil for this purpose is usually a petroleum naphtha, boiling between 110° and 120° C.,[1] and having the specific gravity of 0·720 to 0·750. As the boiling point lies above that of water, it is possible to extract, *e.g.*, moist bones (for which up to recently petroleum benzine was employed exclusively), the vapours of the boiling naphtha carrying the water vapours with them. Notwithstanding the greater fire risks, naphtha is preferable to carbon bisulphide, for the reasons given

[1] Trotman (*Journ. Soc. Chem. Ind.* 1906, 1202) demands that "benzine" for "degreasing" should distil at 90° to 100° C., and should yield small amounts only below or above these limits. It appears to the author that this specification should only apply to petroleum ether for special purposes, such as degreasing leather. For the extraction of bone fat, petroleum ether (of the boiling points given in the text) is mostly used, although it would certainly be advantageous to avoid as much as possible hydrocarbons boiling above 110° C., as their removal is both difficult and expensive.

already, and for the further reason that it extracts less resinous and gummy matters from the oil seeds, and takes up less colouring matter than does carbon bisulphide. Hence petroleum ether only is used in the extraction of linseed, rape seed, and castor seed.

Of other proposed volatile solvents ordinary **ether** has found no practical application, as it is far too volatile, and hence far too dangerous. **Chloroform**, as also benzol and acetone, are far too expensive, besides offering other drawbacks which prevent their application on a practical scale.

During recent years efforts have been made to introduce **carbon tetrachloride** on a large scale. This solvent has a lower boiling point than the usually employed petroleum ether, and shares with carbon bisulphide the advantage of being heavier than water. Its chief advantage, however, is that it is non-inflammable, and from this point of view it might be considered an ideal solvent. As further advantages are claimed :—its low specific heat, its low latent heat of evaporation, and its low boiling point as compared with naphtha. But these slight advantages are not a sufficient set-off against the high price of carbon tetrachloride. For it must be borne in mind that in the extracting process by means of the solvents the *volume* of the solvent and not its weight must be considered. The specific gravity of carbon tetrachloride being 1·632, as against about 0·750 of petroleum naphtha, it follows that for the same volume of solvent more than twice the weight of carbon tetrachloride must be employed. Since the loss of solvent may be taken as amounting in each case to about 1 per cent of the weight employed, and since carbon tetrachloride costs about three times as much as petroleum ether, it follows that the actual loss, expressed in money value, must be much greater than in the case of petroleum ether. In view of the many conflicting statements as regards the cost of the carbon tetrachloride process the following calculation may be found useful (see table, p. 22) :—

	Calories.
1000 kilogs. of petroleum ether require for heating from the ordinary temperature, say 15° C. to the mean boiling point, viz. 115° C., $1000 \times 0{\cdot}5\ (115\text{-}15)$	= 50,000
To vaporise 1000 kilogs. are required 1000×80 . . .	= 80,000
	130,000
1000 kilogs. of naphtha occupy a volume of 1333·33 ltr. ; hence 1000 ltr. of petroleum ether require for vaporisation . .	97,500

To condense the vapours from 1000 ltr.—on the assumption that the cooling water enters the condenser at the temperature of 15° C. and leaves it with a temperature of 60° C., so that 1 ltr. of cooling water would absorb 45 calories,—there would be required $\frac{97500}{45} = 2167$ ltr. of cooling water.

The same calculation carried out for carbon tetrachloride, using the constants given in the table below, shows that there are required for vaporising 1000 ltr. of carbon tetrachloride, 97,151 calories,

and 2159 ltr. of cooling water for condensing the vapours. The difference in favour of carbon tetrachloride is far too small (even if lower insurance premiums be taken into account) to counterbalance the difference in the cost of the amounts of solvents lost. As a further drawback must be reckoned the fact that carbon tetrachloride attacks iron and copper very severely, especially in presence of moisture, so that suitable extraction apparatus must be lead-lined or tinned. In the author's opinion the carbon tetrachloride installations in use, including those made of "homogeneously lead-lined" metal, have not been worked long enough to demonstrate such durability as must be demanded of proper plant, for it is well known that lead is not a good material to withstand the corroding action of hydrochloric acid. In addition to the drawbacks enumerated, it must not be forgotten that carbon tetrachloride exercises on the workmen a physiological action similar to that of carbon bisulphide. Nevertheless, several installations have been erected recently in extracting works, notably in Marseilles. It is contended that the bone fat produced with the aid of carbon tetrachloride is of better quality than that obtained with the aid of petroleum ether. Samples which the author has had occasion to examine bear this out, and the explanation would seem to be given by the fact that the extraction with carbon tetrachloride takes place at a lower temperature than is the case with benzine. The freshness of the bones employed, and their freedom from foreign substances, such as nails, etc., may, however, have had a greater influence than the nature of the solvent. According to reliable information given to the author, the employment of carbon tetrachloride has been abandoned in Marseilles.

At the present time the choice still lies practically between carbon bisulphide and petroleum ether. In order to enable the reader to carry out calculations such as have been given above, the following table is appended :—

	Chemical Formula.	Specific Gravity at 0° C. (Water 4° = 1.)	Boiling Point. °C.	Specific Heat.	Latent Heat of Evaporation. Calories.	Vapour Density.	Vapour Tension at 15° C. Millimetres.
Carbon bisulphide	CS_2	1·292	46·0	0·157	79·9	2·63	250
Petroleum ether	...	0·750 (at 15° C.)	110-120	0·5	80		
Carbon tetrachloride	CCl_4	1·632	76·5	0·21	46·4	5·3	67·1

Other non-inflammable solvents are being recommended at present, such as dichloro-ethylene, $C_2H_2Cl_2$, boiling point 55° C., specific gravity 1·25; trichloro-ethylene, C_2HCl_3, boiling point 88° C., specific gravity 1·47; perchloro-ethylene, C_2Cl_4, boiling point 121° C., specific gravity 1·62; tetrachloro-ethane, $C_2H_2Cl_4$, boiling point 147° C., specific gravity 1·60; and pentachloro-ethane, C_2HCl_5,

boiling point 159° C., specific gravity 1·70. No statement can, however, be made as yet with regard to their applicability on a practical scale.[1] Nor are any practical results known confirming the advantages which have been claimed for liquid sulphurous acid, proposed by *W. Grillo* and *N. Schroeder* (German patent 5360, 1889), and liquid carbonic acid claimed by *A. Sachs* (German patent 163,057, 1904). With regard to acetone and its higher homologues as solvents cp. Vol. III. Chap. XVI.

The type of apparatus employed on a large scale depends on the temperature at which the extraction is carried out. If the extraction is effected in the cold (a procedure which must be considered preferable as regards fire insurance in the case of inflammable solvents), the seed is placed in a series of closed vessels through which the solvent percolates on the counter-current system. The battery of vessels is so arranged that any one vessel can be made the last of the series, ready to discharge the extracted meal, and to be refilled with fresh meal, so that, with the exception of the time required for discharging and recharging, the process is a practically continuous one. The solution of extracted oil or fat in the solvent is then transferred to a steam-heated still, where the solvent is driven off, and recovered by condensing the vapours in a cooling coil, to be used again and again. The traces of volatile solvents retained by the oil or fat are driven off by a current of open steam, which is blown through the oil or fat in the warm state.

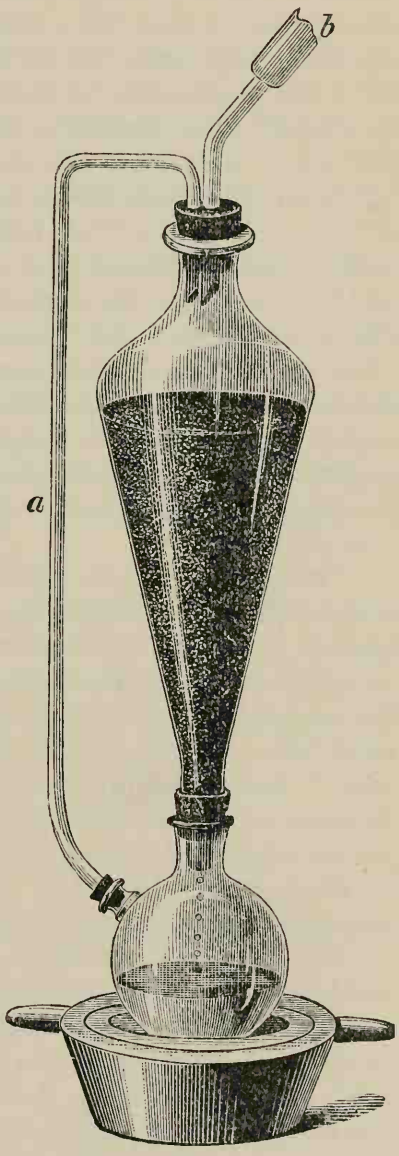

Fig. 7.

The extracting processes in the hot are carried out in apparatus the principle of which is illustrated by Fig. 7. (It should be noted that the condenser is not shown.)

[1] It has been pointed out ("Chem. Fabrik Griesheim-Elektron," *Chem. Zeit.* 1908, 256) that trichloro-ethylene appears to exercise a much stronger narcotic power than carbon tetrachloride, and that it attacks iron to such an extent that oils and fats obtained in an extractor with this solvent are deeply coloured by iron compounds. The attack on iron, however, is not so serious that iron apparatus could not be used for "off-coloured" products. The same holds good of dichloro-ethylene and perchloro-ethylene.

The tetrachloro-ethane and pentachloro-ethane, however, are unsuitable bodies because they easily give off hydrochloric acid when in contact with metals. Although the

More elaborate forms of apparatus employed on a large scale are designed on the principle involved in the *Soxhlet* extractor. The extraction thus takes place uninterruptedly, with a limited amount of solvent charged once for all into the apparatus. When the seed is deemed completely exhausted, the vessel containing the seed is disconnected by closing taps between the oil-containing vessel and the condenser, so that the volatile solvents can be immediately distilled off and condensed, whilst the meal is freed from the last traces of volatile solvents by open steam and the seed-containing vessel is emptied and recharged with fresh seed. More compact still are extractors illustrated by that form of laboratory apparatus in which the meal-containing vessel is placed inside the flask charged with the solvent. Thus in some form of extractors a basket containing the crushed seed is placed on a support at some height above the bottom of the vessel, in other forms the seed is placed in trays arranged one above the other. The vessel is then charged with the solvent, so that, on heating, the vapours of the solvent pass through and around the seed, whilst that portion which leaves the vessel in the form of vapour is condensed in a separate condenser, from which the liquefied solvent falls back again to percolate the seed. Finally, when the meal is exhausted, the solvent is driven off, condensed, and collected in a separate vessel.

Frequent attempts have been made to introduce a really continuous process of extraction. On the principle of the counter-current system, the mass to be extracted is moved continually in a series of tubes or vessels through the solvent, so that at the one end of the apparatus the solvent charged with fat is run into the distilling apparatus, whereas at the other end of the battery the extracted meal is discharged into a vessel to be freed from the adhering solvent. Apparatus of this kind have been patented by *Stevenson* (English patent 28,310, 1902), *E. Bataille* (French patent 319,204), *G. Mitchell* (German patent 119,134), and others. But hitherto, none of these apparatus have met with extended use.

Since apparatus of the type described here are illustrated in the catalogues and advertisements of engineering firms, no useful purpose can be served by reproducing them in this work. Nor does it appear necessary to enumerate the very large number of patents which have been taken out during the last twenty years. For fully illustrated abstracts of these patents the reader must be referred to the volumes of the *Journal of the Society of Chemical Industry*.

Volatile solvents are used in practice for the extraction of seeds such as linseed (in very small quantities), rape seed, castor seed. They are also employed for extracting oil from damaged seed (sesamé) which would not yield edible oil, and from damaged cakes and from cakes which are unfit as cattle food (olive pulp, etc.). Considerable

addition of oil of turpentine, which absorbs hydrochloric acid, is said to obviate the destructive effect on iron (German patent 185,374), the suitability of these solvents on a large scale must be left an open question until practical results are available. It need, therefore, only be added that the makers of these chloro-compounds controvert (*Chem. Zeit.* 1908, 529) most of these statements.

quantities of cocoa nut oil and palm kernel oil are prepared by extraction, where the oil is more valuable than the meal.

The seed for treatment with volatile solvents is prepared in a similar manner as for pressing, except that the seed is not reduced to a fine meal, which would prevent the free percolation of the solvent through the mass. Since extracted oil can never be used for edible purposes, the preliminary cleaning of the seed is not carried out as carefully as is done in the case of seeds destined for the manufacture of edible oils and fats; nor is the preliminary warming of the seed necessary, as the moisture contained in the seed does not offer a serious obstacle to thorough extraction. In the case of olive pulp, however, the removal of the bulk of water by drying is imperative.

The removal of the solvent from the extracted seed offers difficulties, as the meal very tenaciously retains the solvent. If open steam be passed into the mass, to drive off the last traces of the solvent, the meal suffers loss in feeding value—provided such meal can be used as cattle food (see below). It is therefore preferable to dry the meal in special apparatus, similar to those used in breweries for breaking up and discharging the refuse, the seed being dried in shallow layers while it is being continually turned over by a mechanically actuated raking fork.

In order to avoid drying, *Bergman* and *Berliner* (German patent 161,648) suggest displacement of the solvent (French patent 335,964) by washing the extracted mass with acidulated water, or with dilute salt solutions. Whereas this process might be useful for substances like leather, etc., it is entirely unsuitable for meal from oleaginous seeds. In a later patent *Berliner* (German patent 197,725) suggests heating the oil- or fat-containing material with the same oil or fat until the water is driven off, as a preparatory operation to the extraction with volatile solvents.

The extensive use of the extraction process in the treatment of olive residues and bones has been referred to above. In the last few years notable efforts have been made to extend the extracting process to waste products, such as residues from the preparation of whale oil, seal oil, and fish oil, also to the extraction of tanned leather, and of all kinds of fat-containing refuse, such as offal, garbage, greasy rags, etc. (cp. Vol. III. Chap. XVI.).

The fact that it is not necessary to dry the substances previous to their extraction with petroleum ether has been made use of by several patentees. Thus, *Kaleczok*[1] first suggested treating bones, without drying them, with benzine vapours to extract the fat, the condensed vapours of benzine and water being separated in a special vessel. Whereas in this case only small quantities of water are present, the extraction of substances containing considerable amounts of water, such as fruits, with benzine, chloroform, carbon tetrachloride, carbon bisulphide, acetone, and ether is claimed by *Nass-Extraction*,

[1] German patent 81,560.

G.m.b.H. (German patent 179,449, 1902). The patentees distinctly exclude petroleum ether as offering serious drawbacks to this treatment.

With regard to the merits and demerits of the last two classes of processes described—expression and extraction—the adoption of either will largely depend on local factors and on the purpose for which the resulting products are intended.

It is obvious that extraction processes cannot be employed for the preparation of edible oils and fats, for however carefully the last traces of solvents may be removed, there is left sufficient to impart to the oil or fat a nauseous taste, rendering it entirely unfit for consumption.

Extracted oils and fats can, therefore, only be used for technical purposes.

The extracted meal should also be considered as unfit for cattle feeding, notwithstanding the many statements of interested parties that the meal is fit for this purpose, and possesses even a greater value than expressed cakes on account of its higher proportion of albuminoids and carbohydrates when contrasted with press cakes. The oil or fat in an expressed cake has undoubtedly a certain value from a stock-raising point of view, whilst extracted meal to which is added so much oil or fat as to equal the proportion contained in the pressed cakes has not the same nourishing value. This holds good even if we leave out of account the contamination of the meal with the non-removable portion of the volatile solvent. In Germany extracted meal, especially rape meal from good Indian seed and palm kernel meal, is being somewhat largely used as food for cattle, in admixture with press cakes (manufacture of compound cakes). It is stated that some extracted meal is put into cakes also in this country ; but this practice must be condemned, and the bulk of the extracted meal finds its proper use in manuring the land.

Wherever the cake is the main product, the process of expression will commend itself as the more advantageous one. With regard to those fruits and seeds, however, the fatty material of which forms the main product, as in the case of palm kernel oil and cocoa nut oil, the economical factor militates to a much smaller degree against the extracting process, especially when it is possible to dispose of the extracted meal for feeding purposes.

In special cases, notably so in the manufacture of olive oils, a combination of the two processes commends itself. The combined method consists in expressing most of the oil for edible purposes, etc., and then extracting the partially expressed material with volatile solvents, in order to recover the oil left in the press cakes. This combined process is known on the Continent under the name "mixed process" (*huilerie mixte*).

Commercial Preparation of Waxes

The most important waxes, from a commercial point of view, are the *liquid* waxes — sperm oil and Arctic sperm oil. These are prepared on a large scale in the same manner as the animal oils (see pp. 2-4). In the case of sperm oil from the head cavities, the solid wax, spermaceti, is recovered by processes described below under "demargarinating." With regard to the *solid* waxes, frequent attempts have been made to obtain wool grease, the raw material for the manufacture of wool wax (lanoline), from raw wool by extracting with volatile solvents. For this purpose methods described above, under process 3, have been employed, and the solvents actually used were carbon bisulphide and petroleum ether. Recently also carbon tetrachloride has been recommended, but it does not appear to have been used on a large scale. As the wool fibre suffers under the treatment with solvents, the extracting process is used to a very limited extent only. Most of the wool grease is obtained by scouring the wool with soap, or solutions of alkaline carbonates, or both. This process may therefore be likened to the first process described under the heading, "Commercial Preparation of Oils and Fats."

Although beeswax forms an important article of commerce, the preparation of the crude wax must be considered a kind of home industry in which such simple machinery as a hydro extractor, mostly worked by hand, for separation of the honey from the comb, is used. In beeswax candle works, where crude wax is refined, the accumulated residues are subjected to pressure in a hydraulic press, or (and) finally extracted with volatile solvents. The apparatus used in this case is fashioned upon the plant described under processes 2 and 3 under "Commercial Preparation of Oils and Fats."

The preparation of the other animal waxes, and that of the vegetable waxes, remains an industry in which hand labour is almost exclusively employed.

Refining and Bleaching Oils, Fats, and Waxes

The oils and fats prepared by any of the methods detailed above from perfectly fresh ("sweet") material are, in their fresh state, practically neutral. If care be exercised in the process of rendering animal oils and fats, or in the expressing of vegetable oils from fruits or seeds, the products are frequently sufficiently pure to be immediately worked up in those manufacturing processes in which they are used as raw materials. Cases of this kind are tallow, cocoa nut oil, linseed oil. Even edible oils and fats, such as cod liver oil, olive oil, suet, lard, and goose fat, were formerly frequently delivered to the consumer immediately after preparation. The same remarks apply in a general way to the preparation of waxes.

The majority of oils and fats, especially those prepared at a somewhat elevated temperature, contain as a rule mucilaginous

matter, colouring matters, and other impurities, as also free fatty acids, apart from gross mechanical impurities such as fibres, etc. They further contain, as a rule, small proportions of moisture, which cause them to appear turbid in their liquid state.

Except in those cases where the colouring matter can only be removed by treatment with chemicals (cotton seed oil, palm oil) a considerable amount of the impurities is eliminated by a process of spontaneous clarification, the oils and fats being allowed to rest for some prolonged time, when the moisture and mucilaginous matter, etc., settle out. A notable example is furnished by linseed oil, which undergoes on prolonged storage ("tanking") a spontaneous purification, in consequence of which its drying properties are considerably improved (see Chap. XIV. "Linseed Oil"). This self-purification is greatly assisted by the low temperature to which the oil in the store tanks is exposed in winter, the mucilaginous matter being much more insoluble at temperatures below zero than at the ordinary temperature. (The application of artificial cooling for this purpose has been patented by Niegemann, German patent 163,056. Cp. also English patent 10,326, 1905, T. Buchanan: Rapidly heating and rapidly cooling linseed oil.)

Naturally this method can only be applied to those oils which remain liquid at temperatures below zero (Chap. XIV. "Drying Oils"). In other cases the mucilaginous substances are coagulated at temperatures near the boiling point of water and thus settle out more readily. Therefore, washing the oils and fats with boiling water usually leads to a considerable improvement in quality. Thus medicinal castor oil is refined by treatment with steam alone (see Chap. XIV. "Castor Oil").

In modern establishments the process of clarifying is much shortened by filtering the oils and fats through a filter press (or other kind of filter) at a suitable temperature, or brightening them by blowing with air. In many cases these or similar methods suffice for the production of commercial oils and fats.

Free fatty acids, if present in the crude oils and fats, of course remain dissolved in the neutral glycerides. It is therefore evident that oils obtained by such simple methods of purification can only be used in those industries where the presence of free fatty acids offers no serious objection, such as in the candle-making and soap-making industries. In other industries exception must be taken to the presence of free fatty acids. Thus tallow and olive oil containing a high proportion of free fatty acids are unfit for lubricating purposes; and rape oil containing a high percentage of free fatty acids is unsuitable as a burning oil. In such cases the free fatty acids must be removed by treatment with alkalies or alkaline earths.

The highest grade of purity is demanded of products intended for *edible purposes*. In order to attain this object not only must the raw material (seed, fruit, animal tissue) be carefully selected, and worked up in as fresh a state as possible, but the process of rendering must be carried out with especial care. It has been shown above (Vol. I. Chap. I.) that contact of oils and fats with the organic matter

from which they have been obtained (marc of fruit or animal tissues or other nitrogenous substances such as casein) leads to rapid formation of free fatty acids, which in their turn seem to dissolve foreign matters. Therefore not only rapidity in the treatment of fresh material but also the greatest cleanliness is required in the preparation of *edible oils and fats*. Exclusion of air so as to prevent deterioration through oxidation is of the greatest importance for readily oxidisable oils such as cod liver oil. But even more resistant oils, such as cotton seed oil, lard oil, etc., intended for edible purposes, should not be exposed to the air in thin layers at elevated temperatures.

In order to remove colouring matters, edible oils and fats are filtered over charcoal or over natural absorbent earths, such as fuller's earth,[1] Florida earth, etc. Not all kinds of earth are suitable for this purpose. Different kinds of earth found in different parts of the world differ considerably in their action. Thus fuller's earth mined in England is preferable to Florida earth, which, though extremely suitable for mineral oils, is frequently inoperative if applied to vegetable oils and fats. It is impossible to state general rules, for here, as is so frequently the case in the oils and fats industries, each individual oil and fat must be studied separately as to the most suitable condition of the powdered earth, as to the best temperature and the length of treatment, all of which conditions exercise a considerable influence in the bleaching (refining) processes.

With the exception of alkalies or alkaline earths for the removal of small quantities of free fatty acids (and in the case of edible cotton seed oil for the removal of the colouring matter), which may be present in the crude oils and fats, no chemicals must be used in the purifying of edible oils and fats, and even this mild treatment with chemicals is avoided by some patentees (see Vol. III. Chap. XV. "Vegetable Butter"). Notwithstanding the large number of patents which claim effectual purification by means of chemicals, no chemically treated oil or fat can be looked upon as a product fit for consumption. Methods for the preparation of edible oils and fats, which will be described in Vol. III. Chap. XV., embrace, therefore, exclusively (if we except the treatment with alkalies or alkaline earths) physical methods—such as washing with hot water, filtering over animal char or fuller's earth, etc. Where required, it is preceded by a process of deodorisation, as in the case of edible cocoa nut oil, which consists in the purification by means of steam. (For further information, see Vol. III. Chap. XV. "Edible Oils and Fats," "Vegetable Butter.")

The waxes being unfit for edible purposes, no such elaborate process of refining is required as in the case of edible oils and fats.

Nor do oils and fats destined for commercial purposes require such extreme care in refining as do the edible qualities. The removal of

[1] A hydrosilicate is being advertised under the name "German fuller's earth" (cp. E. Graefe, *Petroleum*, 1907, 292), and appears to be recommended also as a "soap filler" under the name "Blanchin."

the free fatty acids, as also the improvement of the colour, if need be, by filtering over char or fuller's earth, is carried out in a similar manner with oils and fats intended to serve as burning oils, paint oils, lubricating oils, etc. (see Vol. III. Chap. XV.). Since the taste is not of paramount importance in judging the quality of commercial oils and fats, bleaching by exposure to the *air* and *sunlight* can be resorted to. Methods of this kind are applied to linseed oil for artists' purposes, as also to the bleaching of beeswax (see Chap. XIV. "Beeswax").

Crude oils and fats, as also those beeswaxes which are more or less deeply coloured, require more elaborate processes of refining, and in most cases a treatment with chemicals is resorted to in the first instance.

The greatest possible stress must be laid on the fact that there is no universal method of refining which is applicable to every and any oil, fat, or wax.

In many cases purification by means of sulphuric acid, invented and patented by *Charles Gower* in 1792 (and frequently ascribed to *Thénard*), is still usefully employed, as in the refining of linseed and rape oils. The method consists in treating the oil or fat with a small percentage of more or less concentrated sulphuric acid—according to the nature of the oil or fat. The acid not only takes up water, but acts on the suspended impurities, carbonising them to some extent, thus causing them to coagulate and separate out in the form of a flocculent mass, which falls down and carries with it mechanically other impurities which have not been acted upon.

As another general method the purification by means of strong caustic soda has been recommended by *Louis C. Arthur Barreswil*, his suggestion being to heat the oil or fat and add 2-3 per cent of a concentrated caustic soda solution. In most cases the purification consisted merely in the removal of the free fatty acids present, the caustic soda forming with the free fatty acids a soap which would either rise as a scum and lift up with it impurities, or fall down to the bottom and carry down the impurities. As a rule, however, this method is a very precarious one, as emulsions are formed which in many cases altogether prevent the separation of the oil (see Vol. III. Chap. XV.). After the treatment with acid or alkali the oils or fats are washed with water to remove the last traces of chemicals, and are then further treated by the physical methods described above.

The number of chemical processes which have been proposed from time to time for the last 120 years, and which are still being copied and perpetuated from old text-books, is almost legion. So long as the chemical nature of oils and fats was little understood, a secret trade in oil-purifying chemicals flourished. But our present knowledge enables us to remove most of these chemicals into the limbo of useless things. Too much stress cannot be laid on the necessity of regarding the bleaching of each individual oil or fat as a problem *sui generis*, and of recognising that the processes adopted

on a manufacturing scale must vary greatly with the nature of each individual oil or fat. In this chapter it is only intended to give a very general survey of this subject. For the processes applied in practice the reader must be referred to the individual oils, fats, and waxes enumerated in Chapter XIV., as also to Chapters XV. and XVI. (Vol. III.). It must therefore suffice here to glance very briefly at the chemical methods employed on a large scale.

Bleaching by the aid of **chemicals** requires great circumspection, the object of bleaching being merely to remove or destroy foreign substances, which impart an objectionable colour, or other undesirable properties, to the oil or fat. The chief attention of the operator must therefore be directed to so treating the raw material that the fatty matter itself is not acted upon. For this purpose the amount of chemicals must be limited to the smallest possible quantity, the temperature at which they are allowed to act must be as low as possible, and the time of interaction must be as short as possible.

General methods of bleaching, the applications of which will be described under the headings of those individual oils and fats for which they are most suitable, are: (1) bleaching by means of oxygen; (2) bleaching by means of chlorine.

(1) The methods of bleaching by oxygen include all those which aim at the bleaching by exposure to the air and to sunlight (see above), and where oxygen or ozone is introduced in the form of a gas, or is evolved by chemicals. Under the head of ozone would also fall those processes where ozone is generated by electrical methods, as in *de Hemptinne's* process (see Chap. XV. "Fish Oil"). Bleaching by means of oxygen gas or ozone is still too uncertain a process to be widely used on a large scale, although it is practised with success in some special instances. Bleaching by oxygen *in statu nascendi* is chiefly effected by employing manganese dioxide or potassium bichromate (less frequently permanganate), and sulphuric acid.

The chemical reactions involved are expressed by the following three equations:—

$$(1)\ MnO_2 + SO_4H_2 = SO_4Mn + H_2O + O;$$
$$(2)\ Cr_2O_7K_2 + 5SO_4H_2 = (SO_4)_3Cr_2 + 2SO_4KH + 4H_2O + 3O;$$
$$(3)\ Mn_2O_8K_2 + 4SO_4H_2 = 2SO_4Mn + 2SO_4KH + 3H_2O + 5O.$$

Sodium peroxide,[1] calcium peroxide, as also persalts[2] (perborates, persulphates, percarbonates of sodium or potassium), organic peroxides (benzoyl peroxide, acetyl peroxide, acetone peroxide), have been recommended as effective bleaching agents, but no definite statement can be made as to their usefulness or superiority over the reagents named above.

(2) In the processes of bleaching by means of chlorine, bleaching powder, chloride of lime, or potassium bichromate (less frequently

[1] Cp. L. Vanino, *Das Natriumperoxyd*, Hartleben, Vienna, 1907.

[2] *Vereinigte Chemische Werke*, French patent 377,720; 378,515; Germ. patent 200,684.

permanganate) and hydrochloric acid are used. The following three equations represent the chemical reactions involved :—

(4) $Ca(ClO)_2 + 4HCl = CaCl_2 + 2H_2O + 4Cl$;
(5) $Cr_2O_7K_2 + 14HCl = Cr_2Cl_6 + 2KCl + 7H_2O + 6Cl$;
(6) $Mn_2O_8K_2 + 16HCl = 2MnCl_2 + 2KCl + 8H_2O + 10Cl$.

Recently a number of reducing agents, such as sulphites and hydrosulphites, have been placed on the market under fancy names, and are recommended as effective bleaching agents for oils and fats. To this class would seem to belong the "formaldehyde-hydrosulphites" and "sulphoxylates."[1]

It may be repeated that no general rule can be laid down as to which process should be employed in each given case, although it may be stated that tallow is best bleached by means of manganese dioxide, and palm oil by means of bichromate and hydrochloric acid.

The object of bleaching is not only to remove colouring matters for the time being, but to remove them so efficiently that the colour, or even a dark shade, does not "revert" some time after the fat or oil has been bleached. Patents claiming to effect this object appear annually in great numbers, and disappear again when experience has shown that the colouring matter does "revert," to a larger or smaller extent, after the material has, *e.g.*, been converted into soap. Thus one of the simplest and most frequently practised processes, that of bleaching tallow, does not lead to soaps as good in colour as those made from freshly rendered tallow. Not only, therefore, must each kind of oil or fat be considered a special problem, but frequently different varieties of one and the same oil or fat are apt to cause the same difficulties as would a new individual. To mention an example, the bleaching of the softer kinds of palm oil, such as "Lagos" or "Old Calabar," offers very little difficulty. But the hardest kinds of palm oil, such as "Congo" oil, have hitherto withstood all attempts to bleach them.

In conclusion it may again be emphasised that, in the absence of careful experiments, it is impossible to state which method of bleaching will be successful in each given case. There is still a wide field open for the application of proper processes for the removal of impurities and colouring matters, without running the risk of attacking the glycerides themselves. Even in the case of the more resistant waxes great circumspection is required, as is evidenced by the different properties of beeswaxes bleached by different processes. (See Chap. XIV. "Beeswax.")

Demargarinating Oils and Liquid Waxes. Separation into "Stearine" and "Oleine"

From some oils and liquid waxes there separate out on standing solid glycerides and solid waxes respectively. The separated

[1] Metz and Clarkson, English patent 11,983, 1906.

glycerides are commercially known under the name of "stearine," or "margarine" (cotton seed stearine, *margarine d'arachide*). In some cases this deposit is objectionable, especially so in the case of oils for table use. An important part in the sequence of the refining operations of such oils is therefore played by the processes aiming at the removal of the solid portions. The simplest demargarinating process, which is still being used to some extent, consists in storing the oils in capacious vessels in a cool place, when the solid glycerides or waxes, as the case may be, separate out as a deposit, so that the clear limpid oils can be drawn off from the upper parts of the vessels.

Where the solid glycerides separate out in a crystalline form, this slow and cumbersome process can be shortened by cooling the oils artificially. A definite temperature must be carefully maintained for each individual oil. The liquid portion is then filtered off; when the whole has solidified to a magma, the oil is expressed through cloths in a hydraulic press. In other cases where the solid glycerides separate out in a gelatinous form, and filtering or pressing is unavailable (see Vol. II. Chap. XIV. "Arachis Oil"), the old process of sedimentation must be resorted to. (Cp. also Chap. XIV. "Lard Oil"; Vol. III. Chap. XV. "Edible Cotton Seed Oil"; Chap. XIV. "Sperm Oil and Spermaceti.")

The limpid oils which remain proof against cold are termed "winter oils." Most of the olive oils are non-congealing oils, whereas some Tunisian and Algerian oils deposit so much stearine that they must be "demargarinated." For the latter purpose, centrifugals[1] have been proposed, but nothing definite can be stated as to their success. It appears to the author rather doubtful whether proper demargarination can thus be effected.

In a wider sense, the term "demargarinating" includes also those processes in which fats which are solid at the ordinary temperature are resolved into two portions of different consistence, generally termed "stearine" and "oleine." As examples may be given the preparation of oleomargarine from tallow (see Vol. III. Chap. XV.), and the separation of oleic acid from stearic acid.

Preserving Oils and Fats

It has been pointed out in the first chapter that oils and fats, if carefully protected from access of light, air, and moisture, retain their state of neutrality indefinitely, and in confirmation the fact was adduced that fats buried with the mummies in Egyptian tombs had remained neutral for several thousand years.

In practice it is, of course, impossible rigidly to exclude contact with air during handling, and it is a matter of daily experience, most noticeable in the case of edible oils and fats, that in course of time they turn rancid.

[1] E. Bertainchand, *Démargarination des huiles de la région de Sfax.* Tunis, 1903.

The cause of rancidity has been traced, in the first instance, to hydrolysis (see Vol. I. Chap. I.), which is accelerated in the case of unrefined oils and fats by enzymes. As regards most commercially prepared oils and fats, the enzymes may be considered as having been destroyed, owing to the elevated temperature which is employed in the refining operations. Where, however, large quantities are prepared merely by rendering at low temperatures (premier jus, lard), the temperature may not be sufficiently high throughout the whole mass to destroy the enzymes in their totality, so that there may remain intact a quantity of enzymes sufficient to cause hydrolysis and subsequently rancidity.

Where the possibility of hydrolysis due to the presence of enzymes is excluded, a small amount of moisture is sufficient, under favourable conditions (the most important of which is a somewhat high temperature), to cause hydrolysis and the rancidity which follows in its wake. It is therefore obvious that it is not only necessary to employ the greatest care in refining, but that it is essential for the preservation of the refined product to exclude as far as possible the presence of moisture. Since, however, even properly filtered fats retain water up to one-half per cent, without revealing its presence by appearing turbid, oils and fats should be stored at as low a temperature as possible.

In the case of edible oils and fats (which demand the greatest care and most scrupulous cleanliness both as regards preparation and packing of the finished article, etc.), cold storage is resorted to as the most effective and most reliable method of preservation.

The low temperature not only arrests the natural process of hydrolysis but inhibits also the injurious action of air on any free fatty acids that may be present. No chemical need be used as a preservative for *pure* oils and fats. In fact, they in their turn are used as preservatives for perishable food-stuffs, since oils and fats do not afford a substratum for the growth of micro-organisms (cp. Vol. I. Chap. I.).[1]

If suitable nutriment is provided, together with the glycerides, as in the case of *butter* and *margarine*, then in addition to all those causes which favour the setting in of rancidity, the micro-organisms exert their deleterious influence on the albuminoids contained in butter and margarine. In these cases, preservatives are not only used largely but are necessary. The most commonly used and entirely unobjectionable preservative is salt. The quantity of salt usually added to butter is sufficient to preserve it for some little time, and for practical purposes, a sufficient length of time. But in consequence of the demand for unsalted butter, and further, owing to the development of the enormous shipping trade in butter from oversea countries —necessitated by the insufficiency of supply from local sources,—the employment of other more powerfully acting preservatives has become almost universal, and has even been permitted by law. Fore-

[1] For a conserving mixture consisting chiefly of oils and fats, cp. S. Fenger, English patent 13,382, 1907.

most amongst these is boric acid. Of course, preservatives of a distinctly poisonous nature, such as sodium fluoride and formaldehyde, are forbidden. With regard to other preservatives, see Chap. XIV. "Butter."

Of minor importance is the preservation of fats by means of such substances as cinnamic acid [1] and gum benzoin. The latter is chiefly used in the pharmaceutical practice to preserve lard.

In this chapter only those oils, fats, and waxes have been considered which are obtained from sound raw material as the main product, or at least as a very important by-product, and thus form staple products of the oil and fat trade. Oils, fats, and waxes obtained as waste products, and the mode of working up these materials, will be treated of in a separate chapter (Vol. III. Chap. XVI.).

[1] Cp. French patent 371,071, P. A. Sparre.

CHAPTER XIV

TECHNOLOGY OF THE NATURAL OILS, FATS, AND WAXES; METHODS OF PREPARING, REFINING, AND EXAMINING THEM, AND DETECTING ADULTERATIONS

In this chapter the individual oils, fats, and waxes are arranged according to the classification outlined in Chapter I. In the first instance, the source and the mode of preparation and refining, wherever this is carried out on a large scale, will be considered; next the chemical composition will be given, as far as it is known. I append in each case tables of the physical and chemical characteristics, as recorded by various observers, and I further add the variations—within narrow limits—of these characteristics, as found in the examination of different specimens of the same kind, wherever these variations are due to difference of source, climate, soil, mode of preparation, race or breed of animal, mode of feeding, and, finally, age of the sample. Thus this chapter gives in a handy form that information which is obtained by applying the methods described in Vol. I. Chaps. V.-XI.

It is hoped that by first scanning the tables the analyst will have placed before him a ready means of identifying any unknown oil or fat which he may have to examine. In each case a discussion of those factors will follow which influence the chemical composition. Next, those adulterants will be considered that are most likely to be met with. Methods of testing for adulteration and determining its amount will also be fully described. It should be mentioned that I have examined in the course of many years most of the products described below; especially those that are of great commercial importance. I did not consider it necessary to record my name in each case amongst the observers. It should, however, be pointed out that the colour reactions to which, in former years, so much importance has been assigned, have been especially examined by me. In the course of these investigations most of the colour tests have been found useless; these have been therefore omitted in this treatise.

The order in which the oils, fats, and waxes are enumerated in the subsections is determined by the magnitude of the iodine value. I have frequently ascertained the iodine values merely for the sake of fixing the order which individual oils or fats should follow. I have, however, not considered it advisable to slavishly follow this principle; hence such oils and fats as are undoubtedly related to one

another are placed together irrespective of differences in their iodine values.

It should further be pointed out that I have carefully scrutinised the numerical values given in the tables. Older numbers which are obviously wrong, or have been obtained by incorrect methods, have been omitted, and only the most reliable numbers have been tabulated.

The technical uses and applications of the oils, fats, and waxes are explained as fully as possible, and statistical data have been added whenever ascertainable, the reliability of the sources of the commercial information being considered of supreme importance.

Thus an attempt has been made to furnish in this chapter, in as concise a form as possible, a complete series of monographs of all known oils, fats, and waxes.

The French, German, and also Italian names of each individual oil, fat, and wax have been added.

A. OILS AND FATS. GLYCERIDES

I. OILS OR LIQUID FATS

1. VEGETABLE OILS

(1) Drying Oils

The drying oils are characterised by their property of absorbing oxygen from the atmosphere, and drying to an elastic skin. It has been pointed out already that the drying power stands in direct proportion to the magnitude of the iodine value, so that the best drying oils are those which absorb the greatest amount of iodine.

Considered chemically, they are characterised by the presence of glycerides of acids belonging to the linolenic and linolic groups, oleic acid forming only a small proportion of the liquid fatty acids. Hence the drying oils do not give the elaïdin reaction. Glycerides of saturated acids are present in small proportions only.

As regards the drying power, there is a slow gradation from the best drying oils down to those standing at the end of the class. The properties of the last-named oils approach more or less those of the semi-drying oils. In the best drying oils, linolenic acid forms a considerable proportion of the liquid fatty acids. The readiest means of ascertaining the amount of the linolenic acids is afforded by the bromide test.

PERILLA OIL

French—*Huile de perilla.* German—*Perillaöl.*
Italian—*Olio di perilla.*

Perilla oil occurs to an extent of 35·8 per cent in the nuts of *Perilla ocymoides*, L., an annual *labiate* indigenous to the East Indies, as also to China (Manchuria) and Japan. It is extensively grown in China and Japan. It is sown in April, blossoms about the end of September, and ripens two weeks later. The seed is known in Japan as *Ye-Goma*, or *Se-no-abura*.

This oil has the highest iodine value of any known fatty oil, and simulates linseed oil in taste and smell. Contrary to expectation, its drying power is inferior to that of linseed oil, although it absorbs up to 20·9 per cent of oxygen. The inferiority in drying may be due to the curious property of the oil of forming drops (like mercury) when spread on a surface.

The specimen examined by *Wijs*[1] contained 0·48 per cent free fatty acids; it gave no colour reaction in the *Halphen* and *Baudouin* tests.

Physical and Chemical Characteristics of Perilla Oil

Specific Gravity.	Saponification Value.	Iodine Value.
At 20° C. (Water 20° = 1.)	Mgrms. KOH.	Per cent.
0·9306	189·6	206·1

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
° C.	Mgrms. KOH.		Per cent.
−5	197·7	284·0	210·6

The perilla plant is cultivated in the Himalayas and extensively in Manchuria,[2] where the oil is used for edible purposes. In Japan the oil is used for mixing with the cheapest kinds of lacquer,[3] as much as 30 per cent of oil being used. It is also employed in the extraction of the last quantities of Japan wax from the berries by mixing the press residues with 10 per cent of perilla oil (cp. "Japan Wax").

LINSEED OIL, FLAX SEED OIL

French—*Huile de lin.* German—*Leinöl, Flachssamenöl.*
Italian—*Olio di lino.*

For tables of characteristics see pp. 44-46.

Linseed oil is obtained from the seeds of the flax plant, *Linum usitatissimum*, L., a native of Central Asia. The principal countries where it is grown in considerable quantities to yield *oil seeds* are Argentina, India, the United States, and Russia. Notable quantities of seed are also produced in Morocco.

[1] *Zeit. f. Unters. Nahrungs- und Genussm.* 1903, 492.
[2] A. Hosie, *Manchuria*, Methuen and Co., 1901.
[3] J. J. Quin, *British Consular Report from Tokio*, 1882.

In the following tables statistical data with regard to the four countries named are given :—

Production of Linseed in the four principal Linseed-growing Countries

Metric tons of 1016 kilograms

Year.	Argentina.	India.	U.S.A.	Russia.	Total.
1892	85,000	487,000	260,000	234,000	1,066,000
1893	120,000	584,000	236,500	363,400	1,303,900
1894	270,000	625,000	177,000	403,500	1,475,500
1895	250,000	326,000	355,000	566,500	1,497,500
1896	185,000	358,000	402,000	703,970	1,648,970
1897	160,000	220,983	273,000	520,552	1,174,535
1898	260,000	446,668	412,500	563,409	1,682,577
1899	250,000	427,894	437,500	316,570	1,431,964
1900	389,951	295,674	475,000	533,877	1,694,502
1901	365,035	336,136	650,000	455,444	1,806,615
1902	763,976	342,624	732,122	542,234	2,380,956
1903	937,601	481,567	682,513	461,314	2,562,096
1904	740,000	571,832	585,013	471,846	2,368,691
1905	591,912	347,400	711,944	421,000	2,072,256
1906	825,764	353,400	626,500	450,000	2,255,664
1907	1,200,000	419,900	646,275	450,000[1]	2,716,175

Exports of Linseed from the four principal Linseed-growing Countries

In metric tons

Year.	Exports from					Imports into Great Britain.	
	Argentina.	India.	U.S.A.	Russia.	Total.	Metric Tons.	Per cent.
1896	230,000	365,810	77,211	481,071	1,154,092	457,362	40
1897	169,092	177,975	26,784	460,038	833,889	349,020	42
1898	142,442	375,908	55,839	220,270	794,459	301,787	38
1899	230,550	416,276	64,641	182,337	912,804	314,148	35
1900	210,693	257,593	52,148	200,643	721,077	309,108	43
1901	336,509	315,378	72,834	55,377	780,098	282,048	36
1902	332,830	311,159	88,585	93,039	825,613	308,331	37
1903	608,307	417,946	18,640	133,257	1,178,150	385,954	33
1904	919,056	527,710	180	76,660	1,523,606	505,519	33
1905	662,264	331,541	22,325	94,643	1,110,773	345,412	31
1906	531,132	221,155	218,436	110,160	1,080,883	286,140	26
1907	831,887	335,214	122,657	78,553	1,368,311	372,537	27

Canadian seed is produced in smaller quantities than in the above-mentioned countries.

These tables may be supplemented by the following table, giving the shipments of linseed to Europe during the years 1900-1906 :—

[1] Estimated.

Shipments of Linseed to Europe

In quarters [1]

From	India		Argentina		Russia and Black Sea	
To	United Kingdom.	Continent.	United Kingdom.	Continent.	United Kingdom.	Continent.
Year.						
1900	636,000	768,000	518,500	616,000	320,000	740,000
1901	758,000	958,000	940,000	844,000	167,000	125,500
1902	661,000	1,031,000	891,500	872,500	210,500	271,500
1903	801,000	1,497,000	1,418,000	1,857,500	282,000	422,000
1904	1,068,000	1,797,000	2,665,500	2,196,000	199,500	207,000
1905	518,000	1,279,000	2,076,500	1,400,500	252,500	247,500
1906	441,000	752,000	1,188,000	1,627,000	243,000	339,000

From	America		Total.	
To	United Kingdom.	Continent.	United Kingdom.	Continent.
Year.				
1900	68,000	207,500	1,542,500	2,331,500
1901	79,500	310,000	1,964,000	2,237,500
1902	105,500	362,000	1,868,500	2,537,500
1903	24,000	74,500	2,525,000	3,851,000
1904	—	1,000	3,934,000	4,201,000
1905	20,000	98,000	2,867,000	3,025,000
1906	281,000	873,000	2,153,000	3,591,000

The quantities taken by France and Germany are detailed in the following tables :—

[1] 1 quarter of Indian linseed = 410 lbs.
1 ,, Argentine linseed = 416 lbs.
1 ,, North American linseed = 424 lbs.
1 ,, Russian linseed = 424 lbs.

Production of Linseed in France, and Imports

In metric tons

Year.	Production.	Imports from				
		Russia.	India.	Argentina.	Other Countries.	Total.
1896	13,288	25,709	56,475	42,546	10,436	135,616
1897	13,306	50,422	27,375	56,615	7,571	141,983
1898	9,069	11,008	67,307	30,235	3,115	111,556
1899	8,769	8,915	76,320	38,023	4,298	127,556
1900	12,515	31,484	32,060	33,300	7,976	104,820
1901	15,519	9,966	40,452	44,621	14,071	109,110
1902	11,426	7,330	40,771	39,846	14,360	102,307
1903	13,826	4,009	61,680	83,014	8,422	157,115
1904	15,438	2,434	67,434	90,064	8,704	168,636
1905	...	2,758	69,044	75,337	9,553	156,642
1906	...	8,233	43,737	73,218	18,809	143,997

Imports of Linseed into Germany

In metric tons

Year.	Imports from						
	Holland.	Russia.	India.	Argentina.	U.S.A.	Other Countries.	Total.
1896	20,390	169,009	69,833	19,241	2,763	7,864	289,100
1897	25,064	172,709	50,841	7,307	2,464	3,869	262,254
1898	23,389	106,106	99,927	30,328	5,472	4,724	269,946
1899	15,256	101,654	114,275	22,938	8,048	3,848	266,019
1900	14,702	107,523	80,405	41,013	17,966	5,962	267,571
1901	9,800	58,950	66,370	74,590	21,740	5,480	236,930
1902	6,990	49,150	74,670	84,340	25,240	5,570	245,960
1903	2,290	47,000	112,540	151,010	4,940	13,370	331,150
1904	1,860	41,920	139,680	262,940	8,010	8,310	462,720
1905	1,040	49,070	110,300	181,930	3,820	7,320	353,480

The area of land on which linseed was grown in the different provinces of India during 1905-07 is stated in the following table :—

[TABLE

Province.		1906-07.	1905-06.	Average of	
				Five Years.	Ten Years.
United Provinces	Pure	315,000	210,900	554,800	472,700
	Mixed	633,000	567,000	565,000	500,000
Bengal		671,800	726,500	728,100	626,900
Eastern Bengal		87,700	103,000	113,000	123,000
Central Provinces and Berar		1,145,200	912,100	729,100	684,900
Bombay		144,200	154,800	298,600	289,900
Hyderabad		664,300	604,500	485,000	421,000
Total	Pure	3,028,200	2,711,800	2,908,600	2,618,400
	Mixed	633,000	567,000	565,000	500,000

Two qualities of Russian seed are recognised in the trade, known, according to their source, as Baltic and Black Sea seed; hence the terms "Baltic linseed oil" and "Black Sea linseed oil." The oil expressed from Indian seed is known as "East India oil." The Baltic linseed yields the best drying oil; this is explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed 5 per cent (and more) of hemp seed or ravison seed are usually present, and Indian seed is always mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. It has been proved that when the Indian linseed is carefully separated from the foreign seeds and then expressed, the oil possesses as good drying properties as best Russian oil. During latter years, more attention having been paid in India to this growing industry, the quality of seed has improved. Argentine seed, yielding the River Plate oil (La Plata oil), being badly harvested, contains much chaff and admixed fibres; if more care were exercised, La Plata oil also would more regularly approach Baltic oil in drying properties. The United States, who until recently have been importing East Indian seed, have so considerably increased the home production that they now rank amongst the exporting countries (Duluth). Canada also is exporting considerable quantities of linseed.

Linseed arriving in this country is sampled and tested by the *Linseed Association*, who ascertain the proportions of linseed and foreign seeds; oil-yielding seeds other than linseed are reported as having half the value of the latter, whereas non-oleaginous seeds are considered as valueless.

[TABLE

Physical and Chemical Characteristics of Linseed Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.[5]		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ Norm. KOH.	Observer.
12	0·939	Saussure	−27	Chateau	−16	Glaessner	190·2-192·7	De Negri and Fabris	173·5-187·7	Thomson and Ballantyne	0·00	Crossley and Le Sueur[2]
15	0·932-0·937	Allen	at −25 "stearine" deposits	Lewkowitsch	to −20		195·2	Moore		Lewkowitsch		
,,	0·9315-0·9345	Thomson and Ballantyne					190-192	Thoerner	173-193	Williams		
,,	0·9342	De Negri and Fabris					192·2-195·2	Lewkowitsch	183-188	Gill and Lamb		
15·5 (water at 15·5 = 1)	0·9316-0·9410	Lewkowitsch[1]					191·5	Crossley and Le Sueur[2]	160-180[3]	Thomson and Dunlop[4]		
,,	0·931-0·938	Gill and Lamb[3]							194·6	Wijs[5]		
,,	0·9337	Crossley and Le Sueur[2]							176·3-201·8	Thomson and Dunlop[6]		
18	0·9299	Stilurell							205·4			
25	0·930	Saussure										
50	0·921	,,										
94	0·881	,,										
99 (water at 15·5 = 1)	0·8809	Allen										

[1] Cp. table, p. 54. [2] East India oil from the Central Provinces. [3] North American oils (*Journ. Soc. Chem. Ind.* 1899, 282).
[4] North American oil (*Analyst*, 1906, 282). [5] Cp. table, p. 56. [6] From picked Baltic (Riga) seed (*Analyst*, 1906, 282).

Physical and Chemical Characteristics of Linseed Oil—continued

Thermal Tests.				Refractive Index.			Viscosity.	
Maumené Test.		Heat of Bromination.						
°C.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
103	Maumené	30·4-31·3	Hehner and Mitchell	15	1·4825	Strohmer	211·7	Crossley and Le Sueur [4]
				20	1·4800-1·4812	Harvey		
		31·4-32·5 [1] [2]	Archbutt	60	1·4660	Thoerner		
104-111	Allen	29·8-30·5 [1] [3]	,,	Oleo-refractometer.				
122-126	De Negri and Fabris	30-33	Bromwell and Meyer [6]					
90-106 [5]	Gill and Lamb				"Degrees."	Observer.		
128-145	Archbutt							
Specific Temperature Reaction.					+48 to +53	Jean		
					+48 to +52	Bruyn and van Leent		
				22	+50 to +54	Permain		
320 to	Thomson and			Butyro-refractometer.				
349	Ballantyne							
313	Jenkins			At °C.	"Degrees."	Observer.		
				20	84-90	Lewkowitsch [7]		
				25	81-87	,,		
				40	74·5	White [8]		
				,,	72·5	Crossley and Le Sueur [4]		

[1] The rise of temperature observed multiplied by two, as 0·5 grm. of oil only was used. [2] Baltic oil. [3] East India oil.
[4] East India oil from the Central Provinces. [5] North American oils. [6] *Amer. Journ. Pharm.* 1897, 145.
[7] Six oils described, *Chem. Revue*, 1898, 211 (cp. table, p. 54). [8] *Journ. Soc. Chem. Ind.* 1900, 1089.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.		Ether-insoluble Bromides.	
Per cent.	Observer.	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.	Per cent.	Observer.
94·81	Crossley Le Sueur [1]	15·5	0·9233	Allen	13·3	Hübl	17	Hübl	198·8	Dieterich	283	Williams	178·5	Williams	1·4546	Thoerner	18-23	Hehner and Mitchell
95·5 mean value	Lewkowitsch	99 (water at 15·5=1)	0·8612	,,	17·5	Allen	24	Allen	196	Thoerner			179-209·8	Lewkowitsch			29·1-31·3	Walker and Warburton
					13·5	Thoerner	Below 13	Dieterich										
		100 (water at 100=1)	0·8925	Archbutt	16-17	De Negri and Fabris	20-21	De Negri and Fabris			Cp. *Chem. Ztg.* 1907, 434	Fahrion,					30-41·9	Lewkowitsch [5]
													Liquid Fatty Acids.					
					Titer Test.								201·4	Tortelli and Ruggeri [2]			Liquid Fatty Acids.	
					19·0-19·4	Lewkowitsch							190·1-193	,, [3]			34·9	Walker and Warburton
					20·2-20·6	,,							208-209·8	Lewkowitsch [4]				

[1] East India oil from the Central Provinces.

[2] Cold-pressed oil, of iodine value 179·4

[3] Italian oils, 1898 and 1899 crop, of iodine values 173·4-176·8.

[4] East India oil, iodine value 184.

[5] Unpublished results.

Corresponding data for the American linseed crop are given in the following table :—

American Linseed Crop in 1907

State.	Acres.	Average Yield per Acre.	Total Yield.
		Bushels.	Bushels.
North Dakota	1,700,000	8·0	13,602,000
South Dakota	480,000	10·0	4,800,000
Minnesota	474,000	10·5	4,978,000
Total for three N.W. States	2,654,000	9·5	23,380,000
Wisconsin	36,000	14·2	515,000
Iowa	20,000	11·5	235,000
Missouri	30,000	10·0	305,000
Nebraska	16,000	11·0	174,000
Kansas	54,000	10·0	539,000
Oklahama	6,000	15·0	90,060
Montana	34,000	13·0	436,000
Idaho	14,000	13·0	177,000
Total for United States	2,864,000	9·0	25,851,000

The proportion of linseed oil in the seed varies with the origin of the seed,[1] and also with the seasons. The figures given below should therefore only be considered as average numbers. It should also be remembered that on extracting seeds with ether larger quantities of crude oil are obtained than on extracting with petroleum ether.

	Oil.
Russian linseed contains	32-38 per cent.
Indian ,,	37-43 ,,
River Plate ,,	35-36 ,,
N. American ,,	36-38 ,,
Levant ,,	37-42 ,,
Hungarian ,,	36-38 ,,
Morocco ,,	36-40 ,,
Sicilian ,,	41-42 ,,

The quantity of linseed oil produced per annum may be taken as being about 35 per cent of the seed.

[1] Experiments made in India with linseed rich in oil, and taken to farms where usually seed yielding a smaller proportion of oil was grown, showed that there was a decline in the percentage of oil. The following table shows some results of those experiments :—

	Original Seed.	Produce of 1905.	Produce of 1906.
Linseed White from Cawnpore	44·62	41·28	39·90
,, ,, ,, Khandwa	44·96	44·18	42·93
,, ,, ,, Damoh	45·34	43·07	43·57
,, Brown from Partabgarh	43·17	40·98	38·31
,, ,, ,, Cawnpore	42·05	40·97	39·43
,, ,, ,, Sholapur	41·13	40·42	38·82

(*Memoirs of the Department of Agriculture in India*, by J. Walter Leather, vol. i. No. 2, p. 38.)

On cold pressing, a golden-yellow coloured oil is obtained, having a pleasant taste, so that it can be used as an **edible oil.** Considerable quantities are being expressed for this purpose in Russia, Hungary, and India. In some parts of Germany also the oil is used either as such, or (as "Leinölschmalz") in admixture with tallow or (and) lard for edible purposes. By far the largest quantities of oil are, however, employed in the arts. In that case the seed is crushed between rollers and then heated up to about 160° F. in the mixing kettle; subsequently the seed is expressed whilst still warm. The oil so obtained has a yellowish-brown hue and is somewhat turbid, due to traces of moisture and mucilaginous matter. The press cakes retain about 10 per cent of oil.

The press cakes are used as one of the most valuable and wholesome cattle foods. It should, however, be noted that they contain a small quantity of a cyanogenetic glucoside, linamarin,[1] which has been shown to be identical with phaseolunatin (a dextrose ether of acetone cyanohydrin), and an enzyme occurring naturally in linseed and in the flax plant. In the presence of water this enzyme acts on the glucoside with production of prussic acid.[2] The temperature to which the linseed meal is heated, preparatory to pressing, suffices to destroy the enzyme. Hence linseed cake as found in commerce is innocuous to the cattle. Cases of cattle poisoning after feeding with linseed cake were, as a rule, hitherto ascribed to an admixture with poisonous seeds, such as castor seed. In the light of the foregoing facts the poisoning may, however, have been due to prussic acid, generated from the cyanogenetic glucoside in consequence of too low a temperature having been employed accidentally in the process of expressing the oil. For this reason the meal obtained in *Anderson's* press (see p. 15) should not be fed to the cattle.

On storing the oil, the moisture and the mucilaginous matter gradually settle out, and the oil thereby acquires a higher value, especially for some technical uses, as in the making of varnish. Such oil, sometimes kept for years, is known as "tanked oil." The suitability for varnish-making purposes is ascertained rapidly by heating the linseed oil in a test-tube. Oil from which gelatinous matter separates is considered unsuitable. Seed pressed in a comparatively fresh ("green") state yields oil containing larger quantities of "mucilage" than seed three to six months old. The gelatinous matter, "mucilage" or "spawn" or "break," contains phosphates and traces of sulphates. *G. W. Thompson*[3] found that a sample of freshly expressed linseed oil heated to 400° F. yielded 0·277 per cent of a precipitate. On washing it with petroleum ether to remove the oil completely, this foreign substance gave 47·79 per cent of ash (0·1177 per cent of the original oil), consisting of 20·96 per cent calcium oxide, 18·54 per cent magnesium oxide, 59·85 per

[1] Dunstan, Henry, and Auld, *Proc. Roy. Soc.* 1906, B., **78**, 145.
[2] Henry and Auld, *Journ. Soc. Chem. Ind.* 1908, 428.
[3] *Journ. Soc. Chem. Ind.* 1903, 1005.

cent phosphorus pentoxide, and traces of sulphate. Other samples of linseed oil gave the following results :—

Description.	Ash. Per cent.
1. Fresh double-filtered raw American linseed oil .	0·1429
2. ,, ,, ,, . .	0·1967
3. Good well-settled ,, ,, . .	0·0609
4. Best American linseed varnish oil ,, . .	Traces

In my own practice I have met with linseed oils containing as much as 0·2 per cent of ash. Such oils give a notable amount of mucilage.

The bulk of linseed oil is at present produced by expression. The main reason for this is that the hot-pressed cake is valuable as cattle food, whilst linseed meal obtained by extraction with solvents could only be used as manure, at any rate in this country.[1] Occasionally linseed has been extracted with solvents, as it was thought that the oil so obtained, being richer in unsaturated acids, and containing less of the mucilaginous matter, would be more suitable for the oil and paint trade. This has, however, not been borne out by practice, extracted oil having been found unsuitable as a paint oil (cp. Vol. III. "Paint Oils"). Moreover, the oil obtained by extracting with carbon bisulphide, petroleum ether, etc., possesses inferior colour and a more unpleasant smell than expressed oil.[2]

As mentioned already, the impurities settle out on long standing, especially in the cold (cp. *Niegemann's* German patent 163,056, p. 28), and the enhanced value of "tanked oil" consists in the comparative freedom of such oil from foreign substances. A more rapid method of removing these impurities is to refine the oil. This is indeed done on a large scale for better-class linseed oil, such as "paint oils." The process consists in treating linseed oil with 1 to 2 per cent of somewhat concentrated sulphuric acid. The charred mass carries down with it the bulk of impurities contained in the crude oil. For the manufacture of the best and finest kinds of linseed oil (artists' oil), the refined oil is subjected to "sun-bleaching," by exposure in shallow zinc trays under glass to the action of sunlight. Powdered lead placed in the trays accelerates the bleaching process. According to *Flatt*[3] linseed oil is also said to be bleached by exposure to the *Cowper-Hewitt* mercury lamp. (Cp. *Genthe*, Vol. III. "Boiled Oils.") Dark linseed oils intended for soft soap are usually bleached in the soap works by treatment with a small amount of caustic potash. The soap which is formed carries down with it colouring matters.

A number of patents have been taken out for the refining of linseed oil by means of ozone; the writer has examined several processes worked on a semi-large scale, but none of them can be said

[1] The German Agricultural Associations distinctly exclude by their specifications cakes containing extracted meal.

[2] Cp. Mittarewski, *Chem. Revue*, 1907, 72.

[3] *Farben Zeitung*, 1907, 108.

to have superseded the usual methods.—Attempts made by the author to remove the solid glycerides from linseed oil on a commercial scale, with a view to obtaining an oil of still higher drying power than is possessed by refined oils, have not proved successful. The value of the method patented by *Hertkorn*[1] for achieving the same object appears, therefore, rather doubtful.

The chemical composition of linseed oil is but imperfectly known. *Mulder* was the first to state that the oil contains about 10 per cent of glycerides of solid fatty acids, consisting of palmitic and myristic acids in about equal proportions. The solid acids separated off by means of the lead-salt-ether method contained, however, notable quantities of liquid acids. *Tolman* and *Munson*[2] found by the same method only 3·88 per cent of solid acids. *Haller*[3] showed recently (by fractional distillation of the methyl esters of linseed oil, see Vol. I. Chap. XII.) that amongst the solid acids of linseed oil there occur also stearic acid in appreciable proportions, and arachidic acid in very small quantities. It may be pointed out that the iodine values of the linseed oils examined by *Haller* varied from 168 to 175. These numbers are somewhat low, and it would therefore appear that linseed oils of higher iodine values must be poorer in solid acids.

The liquid glycerides consist, according to *Hazura* and *Grüssner*, of 5 per cent of oleic acid, 15 per cent of linolic acid, 15 per cent of linolenic acid, and 65 per cent of isolinolenic acid. On calculating the theoretical iodine value of the mixed fatty acids from the composition of the liquid acids as stated, and allowing as a *maximum* 10 per cent of solid acids, a much higher iodine value should result than is ascertainable by experiments. This is shown by the following calculation. A mixture of fatty acids having the following composition :—

	Per cent.
Solid acids	10
Oleic acid	4·5
Linolic acid	13·5
Linolenic acid	13·5
Isolinolenic acid	58·5
	100·0

should absorb, theoretically, 225·89 per cent of iodine. The liquid fatty acids, freed from solid acids, should therefore have the calculated iodine value of 250·9, whereas the highest number found in my laboratory for the liquid fatty acids (prepared by *Tortelli* and *Ruggeri's* method) was only 210. To explain the discrepancy *Fahrion* assumed that raw linseed oil is polymerised during the process of manufacture. This assumption, however, cannot be substantiated.

More recently *Fahrion*,[4] basing himself on a casual remark in a

[1] German patents 129,809 and 137,306 ; cp. *Jahrbuch der Chemie*, xii. 370.
[2] *Journ. Amer. Chem. Soc.* 1903, 960. [3] *Compt. rend.* 1906 (**146**), 259.
[4] *Zeit. f. angew. Chem.* 1903, 1193.

paper by *Hazura*, that very likely isolinolenic hexabromide is soluble in ether, assumes the following composition of linseed oil :—

Unsaponifiable	0·8 per cent.
Palmitic and myristic acids	8·0 ,,
Oleic acid	17·5 ,,
Linolic acid	26·0 ,,
Linolenic acid	10·0 ,,
Isolinolenic acid	33·5 ,,
C_3H_2	4·2 ,,
	100·0

Since, however, higher amounts of linolenic hexabromide have been found than correspond to 10 per cent of linolenic acid, the above composition can hardly be accepted, all the less so as the amount of oleic acid is far higher than can possibly be present in linseed oil. The assumptions underlying the above composition must therefore be accepted with the greatest reserve. More acceptable is *Fokin's*[1] statement that linolic acid predominates amongst the liquid fatty acids, linolenic acid only constituting 22-25 per cent of the mixed fatty acids. This figure is in much better agreement with the yield of ether-insoluble bromides from the mixed linseed oil fatty acids, as obtained in my laboratory, although *Fokin's* statement that the solid fatty acids form 5 per cent only is not in agreement with *Mulder's*, *Fahrion's*, and my own result. From the percentage of ether-insoluble bromides, 42 per cent, I found (see table) the calculated proportion of linolenic and isolinolenic acids (assuming that *both* acids yield an ether-insoluble hexabromide) is 15·4 per cent only, since 100 parts of hexabromides correspond to 36·68 parts of linolenic acids. This amount may be below the true one, but the deficiency is not sufficiently explained by assuming that some ether-insoluble bromide was dissolved out together with linolic tetrabromide ; for experiments which I have made with varying amounts of bromine and ether did not lead to results differing materially from the above-named percentage of ether-insoluble bromide, viz. 42 per cent. The following is an account of an examination of linseed oil carried out in my laboratory :—The sample had the iodine value 190·4 ; it yielded 37·72 per cent of brominated glycerides insoluble in ether, and 8·9 per cent of solid acids of the iodine value 22·3 (by the lead-salt-ether method).[2] After passing the solid acids once more through the same process, 7·5 per cent of solid fatty acids of the iodine value 19·2 were obtained. The mixed fatty acids had the iodine value 194·4, and yielded 38·1 per cent of ether-insoluble bromide of the melting point 176·4° C. Attempts to obtain further quantities of insoluble bromides from the ethereal filtrate failed. The amount found, if calculated to hexabromides, leads to 14 per cent of linolenic and

[1] *Journ. Chem. Soc.* 1902, Abstract I. p. 740 ; *Journ. Russ. Phys. Chem. Soc.* 1902, 501.

[2] By precipitation with lithium acetate Fahrion obtained an acid of iodine value 22 5 ; yield, 7 per cent (*Zeit. f. ang. Chem.* 1904, 1484).

isolinolenic acids. But even on the assumption that linseed oil contains no oleic acid—the dihydroxystearic acid obtained by *Hazura* being regarded as a product of secondary reaction—the iodine value of the mixed fatty acids would only work out to be 182·2, as shown by the following calculation :—

	Per cent.	Iodine Value.
Solid fatty acids of the iodine value 19·2	7·5	1·4
Linolenic and isolinolenic acids . .	14·0	38·4
Linolic acid, by difference . . .	78·5	142·4
		182·2

whereas experiment led to 194·4.

Further light has been thrown on this subject by recent researches of *Fokin*[1] and *Bedford*.[2] *Fokin* reduced the acids obtained after removing the solid acids (by crystallisation) to stearic acid. *Bedford* separated the solid acids and the bulk of the oleic acid from the less saturated fatty acids, by using the barium salt method (Vol. I. Chap. VIII.). 2000 grams of linseed fatty acids were converted into the barium salts, and after treating with $3\frac{1}{2}$ times their weight of a mixture of 95 volumes of benzene and 5 volumes of 95 per cent alcohol at 40° C., 1200 grams of soluble barium salts were obtained. The barium salts of the highly unsaturated fatty acids were then precipitated by adding 95 per cent alcohol. The mixed unsaturated acids so obtained, practically free from solid acids and of most of the oleic acid, could not be resolved by fractional distillation *in vacuo* into several individuals.[3] On treating with *hydrogen* they were completely converted into stearic acid.

Amongst the highly unsaturated acids *Bedford* could not find isolinolenic acid, and he therefore throws doubt on the occurrence of this acid in linseed oil, as also on the existence of isolinusic acid, the hypothetical oxidation product of isolinolenic acid.

On brominating the mixed linseed oil fatty acids *Bedford* obtained 41·6 per cent of ether-insoluble bromide of the melting point 179°-180°, which is in excellent agreement with the number 42 obtained by the author. In *Bedford's* opinion, the mother substance of this ether-insoluble bromide is α-linolenic acid, which can be obtained from the hexabromide by reduction with alcohol and rasped zinc. On brominating again the linolenic acid so obtained, the yield of solid hexabromide is less than before, two experiments having led to 23·3 per cent of ether-insoluble bromide. Hence, *Bedford* is led to assume

[1] *Zeit. f. Elektrochemie*, 1906, 759.

[2] "Über die ungesättigten Säuren des Leinöls." Inaugural Dissertation, Halle a/S. 1906.

[3] The mixed unsaturated fatty acids, after removal of the solid acids by cooling to 0° C., gave on subjecting them to fractional distillation *in vacuo* three fractions the iodine values of which were respectively 201·1, 203·8, 206·6.

that the linolenic acid in linseed oil represents a mixture of two isomeric acids, viz. α-linolenic acid and β-linolenic acid. Of these the α-linolenic acid yields the hexabromide of m.p. 179°-180°, whilst the β-linolenic acid only absorbs four atoms of bromine, and yields a liquid tetrabromide, $C_{18}H_{30}Br_4O_2$. This liquid tetrabromide, which is also formed on brominating linseed oil fatty acids, had been examined already by *Reformatzky*.[1] It had also been obtained by *Hazura*,[2] but was mistaken by him for an ether-soluble isolinolenic hexabromide. *Bedford* ascribes the formation of this tetrabromide to the existence of a β-linolic acid which is isomeric with the ordinary linolic acid (termed by *Bedford* α-linolic acid) as contained in poppy seed oil.[3] According to *Bedford*, *solid* bromo-derivatives are yielded by α-linolenic acid and α-linolic acid, whereas β-linolenic and β-linolic acids yield *liquid* bromo-derivatives. Against this, the serious objection must be raised that poppy seed oil yields no insoluble hexabrominated glycerides (see Vol. I. Chap. VIII.; and this volume, p. 97).

It is evident that further researches are required to satisfactorily establish the composition of the linseed oil fatty acids.[4]

On exposure to air linseed oil readily absorbs oxygen, and when spread in a thin film on a large surface it dries to a neutral substance, insoluble in ether. This substance, the nature of which has not been ascertained hitherto, is termed "linoxyn," and is in its turn further oxidised to a liquid substance—superoxidised oil (cp. Vol. III. Chap. XV. "Oxidised Oils").

The ready absorption of oxygen may explain the occurrence of small amounts of "oxidised" acids in even comparatively fresh oils. When kept protected from moisture, air, and light, linseed oil keeps indefinitely, as shown in the following table, which contains the proportions of "oxidised" acids in some (comparatively) fresh and old linseed oils examined by *Lewkowitsch*[5] (together with a few other "characteristics" and "variables"):—

[1] *Journ. f. prakt. Chemie*, 41 (1890), p. 529. Cp. Vol. I. Chap. III.
[2] *Monatshefte*, ix. (1888), p. 180. [3] Cp. also Fokin.
[4] Cp. also Vol. I. Chap. III. "Linusic Acid."
[5] *Journ. Soc. Chem. Ind.* 1899, 51; *Chem. Revue*, 1898, 211.

[TABLE

	"Oxidised" Acids.	Specific Gravity.	Butyro-refractometer. "Degrees."		Saponific. Value.	Iodine Value.	Acid Value.	Unsaponifiable.
		At 15·5° C. (water 15·5 = 1).	At 20° C.	At 25° C.				
	Per cent.							Per cent.
Oil from finest Calcutta seed, 2 months old	0·65	0·9316	84	82	193·2	170·46	1·3	0·65
Oil from finest Calcutta seed, 3 years old, kept the whole time protected from air and light.	0·7	0·9324	84	81	192·5	174·0	1·3	0·7
Finest St. Petersburg seed, 3 months old	0·88	0·9334	86·5	84	192·2	177·3	1·3	1·1
Finest St. Petersburg seed, 7 months old	0·56	0·9345	87	84	193·1	176·2	1·3	0·98
Baltic (commercial) seed, containing ravison and cameline seed	0·73	0·9343	86·5	84	194·3	170·1	1·3	1·1
Finest and purest Baltic seed, kept 13 years protected from air and light . . .	1·95	0·9410	90	87	195·2	175·8	7·2	1·1

As will be gathered from the preceding table, the proportion of free fatty acids in linseed oil is as a rule small; it rarely exceeds in good commercial samples 1-1·5 per cent. The acetyl value of linseed oil was found by *Lewkowitsch* 3·9. The proportion of unsaponifiable matter varies in commercial samples from 0·3 to 1·2 and even 2 per cent (in River Plate oil), the amount depending on the care with which the manufacture has been carried out[1] in the press-room. The unsaponifiable matter contains phytosterol, but no stigmasterol[2] (difference from rape oil).

On heating linseed oil to 250°-300° C. the specific gravity increases considerably owing to the formation of polymerisation products (see Vol. III. Chap. XV. "Polymerised Oils").

The following tests will be found sufficient for the examination of a sample:—

Specific Gravity. — Linseed oil has a higher specific gravity than any fatty oil that would be used to adulterate it, with the exception of tung oil. Hence a lower specific gravity than 0·93 in a given sample would direct attention to the presence of other fatty oils or mineral oils. A higher gravity would indicate probable adulteration with rosin oils. "Boiled linseed oil" has a higher specific gravity than linseed oil; its presence would in the first instance be detected by the specific gravity test.

The higher the specific gravity of a linseed oil, the more suitable it is for the purposes of the paint and varnish manufacturer. This

[1] A number of determinations of the unsaponifiable matter in linseed oils of different origin has been carried out recently by Niegemann (*Chem. Zeit.* 1904, 97). The percentages varied from 0·83 to 2·1 per cent. Cp. Fendler, *Deut. Pharm. Ges.* 1904, 149; Niegemann, *Chem. Zeit.* 1904, 830; Thoms and Fendler, *ibid.* 1904, 841; Niegemann, *ibid.* 1904, 885; F. Lorentz, *ibid.* 1908, 819.

[2] *Berichte*, 1907, 3682.

is also expressed in a general way by the magnitude of the iodine values. Thus *Wijs*[1] has shown that the specific gravities of a number of linseed oils varied from 0·9310 to 0·9352 as their iodine values varied from 180·1 to 200. On storing, "tanking," the specific gravity increases, as shown by the numbers recorded in the last given table.

The increase must be ascribed to a slight oxidation of the oil, due to the absorption of oxygen, and not to polymerisation.

Iodine Value.—Linseed oil has, with the exception of perilla oil, the highest iodine value of all known fatty oils. Hence the iodine test is the most characteristic one for identifying a sample. The iodine numbers given by earlier observers are much too low, owing to too small an excess of iodine solution having been used. These incorrect values have therefore not been recorded in the above given tables. Correct iodine values are obtained by allowing the *Hübl* iodine solution to act eighteen hours; on using the *Wijs* iodine solution two hours suffice. In either case an excess of iodine must be present, about equal to the quantity of iodine absorbed.

If the iodine value of a sample falls below 170, the presumption that the sample has been adulterated is justified.

The adulteration may have taken place in the seed itself, as it were, the oil having been produced from impure or adulterated linseed (see below).

Somewhat lower values than those given in the table may also be due to an oil having been exposed to the atmosphere, and thereby having absorbed oxygen. This point must be borne in mind before a sample can be pronounced adulterated, as purity of an exposed oil is quite consistent with a somewhat low iodine value.

A high iodine value of itself is, however, not proof of purity, since fish oils, rosin oils, and even drying oils may be readily admixed with linseed oil in considerable quantities, and yet furnish numbers lying in the neighbourhood of those given in the table of characteristics.

The following table, containing the iodine values of linseed oils from specified sources, will be found useful :—

[1] *Chem. Revue*, 1899, 29; *Journ. Soc. Chem. Ind.* 1899, 591.

[TABLE

Kind of Linseed.	Iodine Value of Oil.	Observer.
Baltic	187·7	Thomson and Ballantyne
,, (cp. table, p. 54)	170-177·3	Lewkowitsch
Archangel, Wiatka, Petersburg, Reval, Pernau, Riga, Libau	188·5-200	Wijs
Central Russia (Samara, Steppes)	188·9-189·1	,,
Black Sea, Asoff; Taganrog	176·3-182·5	,,
East India	178·8	Thomson and Ballantyne
East India	170·5-174	Lewkowitsch
,,	182·2-187·5	Wijs
River Plate	173·5-175·5	Thomson and Ballantyne
,,	174·7-182·7	Wijs
,,	179-194	Lewkowitsch
Dutch	191·5-201·8	Wijs
North America	178·1-188·5	,,
,, ,,	160·0-178·8	Gill and Lamb
,, ,,	194-194·6	Thomson and Dunlop
Danube countries	182·1	Wijs
Mixed; from—		
Dutch and Baltic	199·1	Wijs
Various Baltic seeds	198·4	,,
$\frac{2}{3}$ Baltic and $\frac{1}{3}$ Dutch	195·7-197·5	,,
$\frac{1}{2}$,, and $\frac{1}{2}$,,	195·1-195·4	,,
$\frac{2}{3}$ Black Sea and $\frac{1}{3}$ Baltic	185·5	,,
$\frac{1}{10}$,, and $\frac{9}{10}$ River Plate	183·7	,,
$\frac{1}{2}$ Black Sea, $\frac{1}{4}$ River Plate, $\frac{1}{8}$ East India, $\frac{1}{8}$ North America	183·3	,,
$\frac{1}{2}$ La Plata, $\frac{1}{3}$ East India, $\frac{1}{6}$ Black Sea	183·2	,,
$\frac{1}{8}$,, $\frac{3}{8}$,, $\frac{1}{2}$,,	182·9	,,
$\frac{2}{3}$ East India, $\frac{1}{3}$ Black Sea	182·7	,,
Black Sea and East India	181·5	,,
Black Sea, and East India, and North America	181·1	,,
$\frac{1}{2}$ Black Sea and $\frac{1}{2}$ East India	180·9	,,
$\frac{2}{3}$ River Plate and $\frac{1}{3}$ East India	180·1	,,
River Plate, Black Sea, East India	178·7	,,

Bromide Test.—This is an important test for purity. Pure linseed oils yield up to 38 per cent crude ether-insoluble brominated glycerides. From the table given in Vol. I. Chap. VII., it will be noticed that all other drying oils can be readily differentiated from linseed oil by the bromide test, since tung oil, poppy seed oil, safflower seed oil, candle nut oil, either yield no ether-insoluble brominated glycerides or much smaller quantities. If the yield of such brominated glycerides falls below 20 per cent, the presence of other oils than linseed oil may be inferred with certainty. I prefer to brominate the mixed fatty acids (prepared with due precaution against oxidation), as the linolenic hexabromide is easy to obtain in a comparatively pure state, readily ascertainable by its melting point. Linseed oil mixed fatty acids yield up to 42 per cent of bromide melting from

175°-180° C., whereas all other drying (vegetable) oils give much smaller quantities (cp. Vol. I. Chap. VIII.).

Since fish, liver, and blubber oils also yield high percentages of an insoluble bromo-product in the bromide test—most likely *octo*-bromide—the determination of the melting point of the bromides must not be omitted. Linolenic hexabromides from drying oils melt at 175°-180° C. to a *clear liquid*, whereas the bromides (octobromides) from fish, liver, and blubber oils do not melt at these temperatures, they being converted at about 200° C. into a black mass. Experiments carried out in my laboratory proved that it is thus possible to detect admixtures of 10 per cent of fish oil with linseed oil.

The **thermal reactions** which linseed oil gives are not characteristic enough for purposes of identification, and on account of their indefiniteness and the trouble involved in the determination, their employment is not recommended for isolated tests in an analytical laboratory. For special purposes, however, as in a works where a large number of tests must be made rapidly, the *Maumené* reaction, or, better still, the bromine thermal test, may be usefully applied.

Thus oils that are quite pure can be quickly sorted into those which have the lowest iodine value, and hence are suitable for soap-making purposes, and those of a high iodine value which are preferably used in the manufacture of varnish and linoleum. It should, however, be understood that the operator himself must determine the factor which applies to the particular conditions under which the test is carried out. The following table will show how necessary it is for each operator to ascertain the factor which represents, as it were, the personal equation of his experiments :—

Kind of Linseed Oil.	Bromine Thermal Value. ° C. I.	Hübl Iodine Value.	I×5·5.	I×5·7.	I×6·0.	Observer.
...	30·4	160·7	167·2	...	...	Hehner and Mitchell
...	31·3	154·9	172·0	...	...	,, ,,
Raw linseed .	30·55	174·3	...	173·9	...	Jenkins [1]
Old sample .	28·5	167·1	...	...	171·0	,,
...	28·8	177·0	...	...	172·8	Archbutt [2]
American (?)	29·6	177·0	...	...	177·6	,,
...	29·7	177·8	...	...	178·2	,,
East Indian .	29·8	178·7	...	...	178·8	,,
,, ,,	30·45	183·3	...	...	182·7	,,
Baltic . .	31·35	188·5	...	...	188·1	,,
,, . .	31·4	188·8	...	...	188·4	,,
,, . .	31·75	188·8	...	...	190·5	,,
,, . .	32·5	192·5	...	...	195·0	,,

In doubtful cases the determination of the iodine value must of course be resorted to, as only this test furnishes unmistakable results.

[1] *Journ. Soc. Chem. Ind.* 1897, 194. [2] *Ibid.* 1897, 311.

Oxygen Absorption.—The rapidity with which a given sample of linseed oil dries, and the amount of oxygen it absorbs, afford guidance in the valuation of a linseed oil recognised as pure. The commercial value of a sample of linseed oil intended for the manufacture of varnish depends on its drying power, which is determined by the amount of oxygen it absorbs, and also by the time it requires for drying to an elastic skin. The *Livache* method, as also the glass-plate method, may be applied for quantitative purposes, but except in special cases little information can be derived therefrom. It is of far greater importance to observe the time required to dry, and the nature of the skin formed. This test is the one usually applied in technical work. It requires, however, a good deal of practical experience to judge of the quality of an oil by the drying test. The analyst who may be called upon to give an opinion should compare a given sample with an oil of known composition as regards purity and quality, by exposing side by side a number of glass plates coated by means of a palette knife, with a very thin film of oil, so that exactly the same conditions may obtain. A good linseed oil should become dry in less than three days ; it should not be tacky on touching with the fingers, and should yield an elastic coherent skin. Oils containing considerable amounts of unsaponifiable matter or foreign oils will be incidentally detected by this test, inasmuch as these prevent the formation of a good elastic skin.

An important test for judging of the suitability of a linseed oil for making paint oils and varnishes is to heat a few c.c. in a test-tube up to 600° F., that is, until the oil commences to boil up. Good oil should remain clear on cooling (as a rule it will have become lighter in colour). From impure oils mucilaginous matter will separate as a gelatinous mass at the bottom of the test-tube ; in the case of low quality oils this mass will be found disseminated through the oil. Oils of this kind are unsuitable for the manufacture of paint and varnish oils (cp. also Chap. XV. B. iii. and iv.).

Linseed oil, being one of the cheapest fatty oils, is not frequently adulterated with vegetable oils. However, when the price of linseed oil is high, other cheap drying oils, such as safflower oil and candle nut oil, may be employed as adulterants.

Drying Oils.—The presence of considerable quantities of drying oils is indicated by the iodine value being below 175. Their presence would also be indicated in the bromide test, if the yield of the ether-insoluble bromides of the mixed acids falls below 30 per cent. Since tung oil and poppy seed oil yield no ether-insoluble bromides, safflower and walnut oils a very small quantity only, and candle nut oil less than half of the quantity to be expected from linseed oil, the bromide test will be found of greater help than the iodine test.

Cotton Seed Oil.—An inducement to adulterate linseed oil with cotton seed oil will only present itself whenever the latter is cheaper than linseed oil. The presence of cotton seed oil would be detected by a low iodine value. The *Halphen* colour test should be

applied as a confirmatory test (see p. 162), and the melting point of the fatty acids should be determined. In the presence of considerable quantities of cotton seed oil, the titer test will be found considerably above 20° C.

Rape oil would be indicated by a lower saponification value than a normal one (of course, in the absence of unsaponifiable oils). A few per cent of rape oil, such as are frequently present in commercial linseed oil, will not be detected thereby. The test will, however, in many cases afford some guidance as to the excess of foreign seeds in the linseed from which the sample has been obtained.

Fish Oils — Blubber Oils. — Since fish oils absorb fully as much iodine as linseed oil does, and since they yield as much and even more ether-insoluble bromides, the quantitative tests will not give a satisfactory answer.

More decisive results are obtained by taking the melting point of the ether-insoluble bromide of the fatty acids. In the case of pure linseed oil, a white or only slightly yellowish hexabromide is obtained, melting sharply without decomposition at 175°-180° C., whereas the octobromides from fish and blubber oils become dark or almost black at 200° C., and do not melt. Even 10 per cent of fish oil can thus be detected. In doubtful cases the phytosteryl acetate test is reliable for the detection of fish (liver) and blubber oils. The crystals of phytosteryl acetate from pure linseed oil melt at 128°-129° C. (*Bömer* and *Winter*). In the presence of cholesterol the melting point of the acetate is much lower.

Unsaponifiable Matter.—Adulteration with mineral oils and rosin oils is still frequently practised, although these oils are very easily detected. If only one of these two oils be the adulterant used, the specific gravity of the sample alone will indicate the further line of examination. A judiciously prepared mixture of both oils will, however, have the proper specific gravity of linseed oil.

The presence of either adulterant is readily indicated by a low saponification value (below 190); the amount of the adulterant is determined by weighing the unsaponifiable matter. Pure linseed oils contain no more than 1-2 per cent of unsaponifiable matter. If a notable amount of unsaponifiable matter has been found, and the presence of rosin oil be suspected, the polarimetric method will give useful indications. Linseed oil is practically optically inactive—a sample of East India oil, examined in a 200 mm. tube, showed the deviation of 0° 6′ to the right—whereas rosin oil is strongly dextrorotatory (cp. Vol. III. "Lubricating Oils").

Rosin (colophony) is best detected qualitatively by applying the *Liebermann-Storch* reaction. If the colour of the sample be very dark, it is best to warm it with alcohol, so as to extract the bulk of the colophony, and test the alcoholic extract. The amount of rosin can be determined quantitatively by titrating the sample of oil with aqueous normal alkali, using phenolphthalein as an indicator. From the amount so found, there must be subtracted the amount of alkali used for neutralising the free fatty acid in linseed oil—which rarely

exceeds about 3 per cent. Test experiments made in my laboratory with mixtures of linseed oil and rosin proved the correctness of this method. If, however, a large amount of linseed oil fatty acids is present, as in linseed oil soap stock (see Vol. III.), the amount of rosin in the alcoholic extract must be determined quantitatively by *Twitchell's* method.

Linseed oil is very extensively used as stock material for soft soaps; for this purpose those oils are especially employed which have a comparatively low iodine value. The presence of mucilage forms no objection.

The principal application of linseed oil is found in the manufacture of boiled oil for paints, varnishes, lithographic varnishes, and for the manufacture of linoleum. No other drying oil approaches the properties of linseed oil, the drying oil *par excellence*. Hence linseed oil is the best oil for making putty.

The manufacture of **boiled oil**, its characteristics, and detection if in admixture with linseed oil, will be treated of in Chapter XV., as also the chemistry and technology of oxidised linseed oil.

Linseed oil is also used in the manufacture of "Vulcanised Oils" (cp. Vol. III. Chap. XV.), and for extracting india-rubber from "waste rubber." By heating linseed oil with sulphur, the official *oleum lini sulf.* is prepared.

TUNG OIL

(*Chinese Wood Oil, Japanese Wood Oil*)[1]

French—*Huile d'abrasin, Huile de bois de Chine, Huile de bois du Japon.* German—*Tungöl, Ölfirnisbaumöl.* Italian—*Olio di legno del Giappone.*

For tables of characteristics see pp. 63, 64.

Tung oil[2] is obtained from the seeds of *Aleurites cordata*, Müll. Arg. (*Elæococca cordata*, Bl.; *Elæococca vernicea*, Juss.; *E. sinensis*, *Dryandra vernica*, Corr.), a tree indigenous to China and Japan[3] (Japanese, *Abura giri*, *Jani kiri*; Chinese, *Tung Yu*). The tree also grows abundantly in Indo-China, Tonkin, Annam, and Cambodja (Tonkinese, *Cây-trâou*; Annamese, *Cây-dau-son*; Cambodjese, *Doeum-chor-tuc*).

The fruits form a nut, in which three seeds having a hard and an oleaginous kernel are enclosed; hence in China the oil is frequently termed "nut oil."

The composition of tung oils varies somewhat according to their source, and the treatment of the seeds in different localities. Three kinds of seeds are distinguished—yellow (*pay-yu*), drab (*hsin-yu*), and white (*hung-yu*). The seeds are roasted in a flat dish over a naked fire and then broken to powder between stones; finally the mass is

[1] The oil is also known in commerce under the name wood oil, but since Gurjun balsam is also termed wood oil, confusion of tung oil with the ethereal Gurjun oil must be avoided.

[2] First mentioned by the Jesuit D'Incarville (about the year 1735) as a common adulterant of Chinese lacquer. *Paulownia imperialis*, Sieb. et Zucc. (?)

expressed in crudely made wooden presses. The kernels contain about 53 per cent of oil, but the yield of oil amounts to only 40-41 per cent. The cold-drawn oil is pale yellow, and termed white tung oil. This is the variety chiefly imported into Europe. The oil obtained by hot pressing is dark brown, and termed black tung oil. This oil is consumed at home; it has an unpleasant taste, and its odour is more pronounced than that of the white tung oil, which is also somewhat unpleasant. This odour precludes its use for many purposes. The objectionable smell is stated to be absent from oils obtained from seeds freed from all damaged kernels.[1]

Tung oil is also expressed in Madagascar, where the oil is known under the name "Bakoly oil." This name is most likely a corruption of bancoulier (*Aleurites moluccana*).

Intermixed with *Aleurites cordata* there occurs in the Chinese province Fokien *Aleurites Fordii*, Heussl., the seeds of which also furnish commercial tung oil; and it appears that the commercial tung oil is indiscriminately prepared from the seeds of *Aleurites cordata* or *Aleurites Fordii*, or mixtures of the two. The nuts of *Aleurites Fordii* are known under the name "kaloo nuts"; they are poisonous. The oil extracted from the seeds of *Aleurites Fordii* differs very little from the oil from *Aleurites cordata*. The examination of the tung oil from *Aleurites Fordii* carried out in the Imperial Institute[2] gave the following characteristics:—

Specific gravity at 15° C.	0·9404
Saponification value	191·8
Iodine value	166·7
Insoluble fatty acids	94·6 per cent
Titer test	42-42·5° C.
Acid value	2·89

The chief shipments of oil are made from Hankow and Wuchow in China; comparatively smaller quantities are exported from Japan (Hokkaido).

The following table gives the export figures from 1897 (when the first shipments were made to Europe) up to 1901:—

Exports of Tung Oil from Hankow and Wuchow

Year.	Hankow.	Wuchow.
	Tons.	Tons.
1897	13,049	287[3]
1898	19,707	653
1899	21,044	1237
1900	19,653	1456
1901	16,701	1802
1906	28,685	...
1907	23,540	...

[1] Cp. Fahrion, *Zeit. f. ang. Chem.* 1905, 406. [2] *Bull. Imp. Inst.* 1907, 134.
[3] Seven months only.

The home consumption of China is estimated to be at least double the amount of oil exported.

The export from French Indo-China has reached 300 to 400 tons per annum during the last eight years.

The cakes are poisonous, and are therefore only used as a fertiliser, or for the manufacture of lampblack. Poisonous properties have also been attributed by some writers to the tung oil itself, but this is open to doubt (see p. 66 and Appendix).

Tung oil consists chiefly of the glycerides of oleic and elæomargaric acids (Vol. I. Chap. I.). Hence, although tung oil gives in the bromide test 0·38 per cent of a precipitate, its fatty acids do not yield any ether-insoluble bromide (cp. Vol. I. Chap. VIII.). In the elaïdin test an oily layer is obtained resting on the lower, nearly solid product; when stirred up, the whole mass flows.

The freshly expressed oil is free from fatty acids; the samples examined in Europe contain from 4-6 per cent of free fatty acids, calculated as oleic acid. The amount of unsaponifiable matter in the tested samples did not exceed 0·5 per cent.

The characteristic numbers are contained in the two tables, therefore it is only necessary to point out the special properties serving to identify this oil.

The oil is most readily identified by its strong characteristic smell, which is not easily removed. The Chinese variety of tung oil is also characterised by having the highest specific gravity of any known oil with the exception of castor oil, with which it cannot be easily confounded. The Japanese variety of tung oil has a lower specific gravity, viz. 0·933-0·935 at 15·5° C.

The oil is further readily recognised by the manner in which it dries. It possesses even more strongly pronounced drying power than linseed oil, but it differs from the latter in that it gives on a glass plate a dry opaque skin, which is wax-like, but has no elasticity, and hence is not useful commercially.

Hall[1] states that he once obtained a sample of tung oil giving a thin transparent film.

When heated with lead oxide or red lead, the oil gelatinises within fifteen minutes to a light brown mass.

A characteristic property of tung oil is to form a jelly on being heated to 250° C. for a short time, or even when kept at 180° C. for an hour or two. On exposure to the light the oil becomes also solid.[2] The jelly-like mass so obtained possesses some elasticity, is insoluble in the ordinary solvents of oil, and shows no tendency to melt on being again heated to 250° C. The gelatinisation is not due to oxygen absorption, as has been explained by some observers, since the conversion into a semi-solid mass takes place when air is carefully excluded. Further study of the properties of elæomargaric acid, which distinctly differs from linolic acid, may lead to a proper explanation of the curious behaviour of this oil on heating. The change is very likely due to polymerisation of the glycerides (cp. Vol. III. Chap. XV. B ii. (2) "Polymerised Tung Oil").

[1] *Journ. Soc. Chem. Ind.* 1903, 599. [2] Cp. Kitt, *Chem. Rev.* 1905, 242.

Physical and Chemical Characteristics of Tung Oil

Specific Gravity.			Solidifying Point.[4]		Saponification Value.		Iodine Value.		Thermal Tests.		Refractive Index.	
									Maumené Test.		Oleo-refractometer.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Specific Temp. Reaction.	Observer.	"Degrees" at 22° C.	Observer.
15	0·936[1]	De Negri and Sburlati	Below −17	Jenkins	211	Davies and Holmes	165·7	Jenkins	372	Jenkins[6]	+75	Pearmain
									298	,,		
15·5	0·9385	Jenkins			194	Jenkins	149·7	,,				
,,	0·9343	,,			192	,,	159-161	De Negri and Sburlati				
,,	0·9412-0·9418[2]	Lewkowitsch			155·6[5]	De Negri and Sburlati	163·4	Lewkowitsch				
,,	0·933-0·935[3]	Nash			172	,,	155·4-165·6	Williams	Heat of Bromination.		Refractive Index.	
					191·2	Deering			°C.			
					190·7-196·1	Williams	163	Zucker	23·4	Jenkins	At 19° C.	Observer.
									21·4	,,		
					197	Zucker			26·7-27·6	Williams	1·503	Jenkins

[1] Prepared in the laboratory from the seeds. [2] Chinese oil. [3] Japanese oil.

[4] According to De Negri and Sburlati, tung oil obtained by expression solidifies at 2°-3° C., whereas oil extracted by means of carbon bisulphide, after heating to 100° C., yields a crystalline mass solidifying at 32° C. and melting at 34° C. Cloëz (*Compt. rend.* 81, 469), who first observed this phenomenon, explains this by the formation of elæostearin.

[5] Commercial oil. [6] 10 grms. of the sample diluted with 40 grms. of olive oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Thermal Test. Heat of Bromination.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.
96·2	Jenkins	34	Jenkins	37	Jenkins	188·8	De Negri and Sburlati	150·1	Jenkins	21·0	Jenkins
96·3-96·7	Williams	31·2	De Negri and Sburlati[1]	30-31	,,			144·1	,,		
				43·8	De Negri and Sburlati[1]			159·4	De Negri and Sburlati[1]		
				40	Williams			145·0	Lewkowitsch		
				40·3	Nash[2]						
		Titer Test.						Liquid Fatty Acids.			
		37·1-37·2	Lewkowitsch					179·7	Lewkowitsch		

[1] Prepared in the laboratory from seeds.

[2] Private communication.

If a saturated solution of iodine in chloroform or any other solvent be dropped on tung oil, the oil is immediately solidified; and if the oil has been previously dissolved in chloroform, a jelly is obtained. Bromine has no such action on the oil.

Concentrated sulphuric acid gives a black clot with the oil.[1] When 1 grm. of the oil is dissolved in 5 c.c. of chloroform, and 5 c.c. of a saturated solution of iodine in chloroform is added, and the mixture stirred, the whole is converted into a stiff jelly after about two minutes. If 2 grms. of the oil be employed under the same conditions, the jelly is so stiff that it can be granulated.

Tested in *Redwood's* viscosimeter, 50 c.c. of the oil required 1433 seconds as compared with 28 seconds for water.

In *Valenta's test* the temperature of turbidity is 44°-47° C.

In the *sulphur chloride test* 5 grms. of the oil treated in the cold with 2 c.c. of sulphur chloride and 2 c.c. of carbon bisulphide give in $1\frac{1}{2}$ minutes a thick, stiff jelly. (This does not take place when tung oil is adulterated with Gurjun balsam, the ethereal oil of *Dipterocarpus turbinatus*, Zucker.[2]) The *refractive index* of tung oil is much higher than that of any known fatty oil. It should be noted that it cannot be examined in the butyro-refractometer, since its high refraction would place the critical line beyond the 100 degree limit of this instrument (as in the case of rosin oils).

Statements that tung oil is being adulterated with cotton seed oil have not been borne out by the author's experience. Commercial samples examined in this direction have shown throughout the absence of cotton seed oil. A lower iodine number than those registered in the table will readily reveal the presence of cotton seed oil.

Tung oil, on account of its drying properties, might suggest itself as an adulterant of linseed oil; but although it is the most rapidly drying oil known hitherto, it cannot replace linseed oil. In fact, even in Japan itself, linseed oil has not been ousted by tung oil, except for some common purposes, such as paper umbrellas (*Divers*[3]). A few years ago, when tung oil (which is being produced in enormous quantities) was shipped in large quantities to Europe, and was therefore somewhat strongly pressed on the market, a large number of patents were taken out purporting to put tung oil to the same uses as linseed oil, or at least to employ it in admixture with linseed. Yet hitherto very little progress has been made in the technical application of tung oil.

In China and Japan tung oil is used chiefly as a natural varnish for wood, for caulking junks and boats, as a common adulterant of lacquer, and also for lighting. Large quantities are also consumed for water-proofing paper and all kinds of tissues. The oil is further employed in admixture with powdered lime as a mortar. The best kinds of Chinese ink are obtained by burning the oil with a regulated

[1] With regard to the action of acid, sp. gr. 1·688, see Vol. III. Chap. XV. B. ii. (2).

[2] *Chem. Zeit.* 1900, Rep. 156.

[3] *Journ. Soc. Chem. Ind.* 1903, 599.

amount of air. The cold-drawn oil is stated to be used in medicine as an emetic and also as a purgative. (According to *Hertkorn*[1] tung oil is poisonous. Cp. Appendix.)

Further information on the technical applications of tung oil in the paint and varnish industries will be given in Vol. III. Chap. XV. under "Polymerised Oils" and "Oxidised Oils," and "Linoleum Substitutes."

LALLEMANTIA OIL[2]

French—*Huile de Lallemantia.* German—*Lallemantia Öl.*
Italian—*Olio di lallemanzia.*

Physical and Chemical Characteristics of Lallemantia Oil

Specific Gravity at 20° C.	Solidifying Point.	Saponification Value.	Iodine Value.	Reichert Value.
0·9336	− 35° C	185	162·1	1·55

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Iodine Value.
Per cent. 93·3	11° C.	22·2° C.	166

Lallemantia oil is obtained from the seeds of *Lallemantia iberica*, Fisch. et Mey., a plant belonging to the *Labiatæ*, growing wild in the Caucasus, and cultivated in Russia (near Kieff). *L. Royleana*[3] grows wild in the steppes of Turkestan.

The oil belongs to the best drying oils, as is indicated by its iodine value. A sample of the oil spread on a watch-glass dried after 9 days to a thick, resin-like skin. If the oil is heated to 150° C. for 3 hours, complete drying takes place after 24 hours. The absorption of oxygen, determined according to *Livache* (using copper powder), was 15·8 per cent after 24 hours for the oil, and 14 per cent after 8 days for the mixed fatty acids. 10 grms. of the oil at 18° C. mixed with 2 grms. of concentrated sulphuric acid rose to a temperature of 120° C.

In the elaïdin test 10 grms. of the oil, shaken with 5 grms. of nitric acid, specific gravity 1·4, and 1 grm. of mercury, give after three minutes a dark-red dough-like mass.

[1] *Chem. Zeit.* 1903, 635. [2] Richter, *Zeitsch. f. Chem. Ind.* 1887, 230.
[3] *Chem. Zeit.* 1905, 556.

Lallemantia oil is used in Persia, Syria, and Kurdistan as an edible oil and also as a burning oil. It may find technical application as a substitute for linseed oil in the preparation of varnishes.

CANDLE NUT OIL

French—*Huile de bancoulier*, *Huile de noix de Bancoul*, *Huile de noix de chandelle*. German—*Candlenussöl* (*Kandelnussöl*), *Bankulnussöl*. Italian—*Olio di noci di Bankoul*.

For tables of characteristics see p. 68.

Candle nut oil is obtained from the seeds of *Aleurites moluccana*, Willd., a tree widely distributed over the tropics of the eastern hemisphere. The fruits resemble ordinary walnuts in their appearance; their shell is, however, far thicker. The shell is removed by the natives in a primitive fashion by drying the nuts on hot stones, so that the shell can be readily broken by a slight blow with a hammer. The seeds examined in my laboratory contained 62·25 per cent of oil.

In view of the divergent numbers—especially as regards the iodine value—recorded in the table of characteristics, it may be pointed out that the author prepared the oil on a semi-large scale from seeds obtained through a reliable source from the South Sea Islands. Hence the numbers given by *Lewkowitsch*[1] must be accepted as the most correct ones. (Practically identical numbers have been obtained by *Kassler*[2] from Fiji candle nuts, the seeds of which contained 58·6 per cent of oil.) The oil cakes obtained on a large scale by expressing the oil from the crushed nuts had the following composition (*Lewkowitsch*):—

	Per cent.
Oil	8·80
Moisture	10·00
Ash	8·28
Albuminoids	46·16
Cellulose	1·47
Carbohydrates (by difference)	25·29

The ash contained 23·52 per cent potassium oxide, and 53·04 per cent phosphorus pentoxide.

The cold-drawn oil is limpid, colourless, or yellowish, has a pleasant odour and bland taste, but cannot be used for edible purposes on account of its purging properties.

Although the seeds were examined several months after arrival, the extracted oil contained only 4 per cent free fatty acids. Its acetyl value was 9·86, and the proportion of oxidised acids 0·21 per cent.

[1] *Chem. Revue*, 1901, 156.
[2] *Augsburger Seifensieder Zeitung*, 1902, 689.

Physical and Chemical Characteristics of Candle Nut Oil

Specific Gravity.			Melting Point.		Saponification Value.		Iodine Value.		Refractive Index. Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At °C.	"Degrees."	Observer.
15	0·9232	Cloëz	Liquid at −18°	De Negri	184-187·4	De Negri	(136·3-139·3?)	De Negri	15	76-75·5	De Negri
15	0·920-0·926	De Negri			192·62	Lewkowitsch	163·7	Lewkowitsch	20	78·5	Lewkowitsch
15·5	0·92565	Lewkowitsch							25	76·0	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
95·5	Lewkowitsch	13	De Negri	20-21	De Negri	142·7-144·1	De Negri
						Liquid Fatty Acids.	
						185·7	Lewkowitsch

The high iodine value places the oil prominently amongst the drying oils. However, the older statements that this oil surpasses linseed oil in drying properties must be abandoned as erroneous; not only is its iodine value lower than that of linseed oil, but the proportion of ether-insoluble bromides is much smaller. Thus *Walker* and *Warburton*[1] ascertained in the author's laboratory that the oil yields from 7·28 to 8·21 per cent of ether-insoluble brominated glycerides, whilst the fatty acids yield from 11·23 to 12·63 per cent ether-insoluble brominated acids.

Candle nut oil is obtainable in enormous quantities. It is used in its home as a burning oil. It should prove suitable for soap-making, especially for the manufacture of soft soaps. It may also find some application in the manufacture of paint oils and varnishes as a substitute for linseed oil. When the price of linseed oil is high, adulteration with candle nut oil may occur. Its presence would be revealed by a somewhat low iodine value of the sample, and a low yield of ether-insoluble bromides. Smaller quantities than 20 per cent could not, however, be detected by chemical means. In doubtful cases practical drying tests must be resorted to.

Fendler[2] recently examined the seeds of *Aleurites moluccana* from the Cameroons. The kernels contained 6·3 per cent of water and 64·4 per cent of oil. The oil obtained by extraction with ether has a yellow colour and an acrid smell. Its specific gravity at 15° C. is 0·9254; solidifying point, − 15° C.; saponification value, 194·8; iodine value, 114·2; and Reichert-Meissl value, 1·2. The solidifying point of the fatty acids is 15·5° C., and their melting point 18° C.

On comparing these numbers with those given for candle nut oil (p. 68), it will be observed that the iodine value is considerably lower. This is all the more surprising, as *Fendler* states that the oil dries quickly when spread in a thin layer.

Oil obtained from *Aleurites triloba*, Forst., is known in India under the name of

KEKUNA OIL[3] (CANDLE NUT OIL)

The yield of the oil from the seeds is about 50 per cent. The roasted nut forms an agreeable fruit.

The oil is used for soap-making and cloth-dressing.

Aleurites triloba forms one of the best shade trees in Hong Kong, where it grows very quickly. The seeds yielded on examination at the Imperial Institute[4] 60·80 per cent of oil, equivalent to a yield of 19·8 per cent from the unshelled seeds. The following characteristics were ascertained:—

[1] *Analyst*, 1902, 237. [2] *Zeit. Unters. d. Nahrungs- u. Genussm.* 1903, 1025.
[3] *Journ. Soc. Chem. Ind.* 1901, 642. [4] *Bulletin Imperial Institute*, 1907, 136.

Specific gravity at 15° C.	0·9274
Saponification value	204·2
Iodine value	139·7
Reichert-Meissl value	1·98
Insoluble fatty acids + unsaponifiable	96·4 per cent.
Titer test	17·8° C.

STILLINGIA OIL[1] (TALLOW SEED OIL)

French—*Huile de Stillingia.* German—*Stillingigaöl.*
Italian—*Olio di Stillingia.*

For tables of characteristics see p. 71.

Stillingia oil is obtained from the seeds of *Stillingia sebifera*, Willd. (*Croton sebiferum*, L.), *Sapium sebiferum*, Roxb. In the great Chinese centres of the vegetable tallow and stillingia oil manufacture, the tree is grafted and yields fruit superior to that of the wild tree. The latter occurs largely in Formosa, but its cultivation has been entirely neglected hitherto. The mesocarp surrounding the seeds yields, on being steamed, the vegetable tallow of China (cp. below). The oil is obtained by expressing the seeds after freeing them from the vegetable tallow, and is termed by the natives *tsé-iéou* or *ting-yu*. The seeds are said to yield 19·2 per cent of limpid oil, of pale yellow colour. A specimen of seeds examined recently in the author's laboratory yielded 23·29 per cent of oil on extraction with ether. Of the seeds freed from the mesocarp 489 go to make up a weight of 50 grams. The oil has a peculiar smell and taste resembling that of linseed oil and mustard.

The fatty acids separate on standing into a liquid and a solid portion. A specimen of mixed fatty acids examined in my laboratory yielded 25·78 of ether-insoluble bromides of the melting point 171·1° C. (*Lewkowitsch*).[2]

The specimen prepared by *Tortelli* and *Ruggeri* contained 6·15 per cent of free fatty acids (calculated to oleic acid) and 1·45 per cent unsaponifiable matter. A specimen examined by *Nash*[3] contained 3·1 per cent free fatty acids and 0·44 per cent of unsaponifiable matter. 1000 grms. absolute alcohol dissolve at the ordinary temperature 42·8 grms. of the neutral oil, or 48·9 grms. of the oil containing 6·15 per cent of free fatty acids.

The most characteristic property of the oil is that it rotates the plane of polarised light strongly to the left, viz. − 6° 45′ in a 200 mm. tube in a *Laurent* polarimeter, corresponding to − 29·9 saccharimeter degrees. The optical activity of the oil is confirmed by *Nash*.

Stillingia oil has very good drying powers, absorbing 8·72 per cent and 12·45 per cent of oxygen after two and eight days respectively in *Livache's* test. It is used in China as a high-class lighting oil; hitherto it has not been exported.

[1] "Oleum stillingiæ" is vegetable tallow (of China).
[2] *Analyst*, 1904, 112.
[3] *Analyst*, 1904, 111.

Physical and Chemical Characteristics of Stillingia Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Thermal Test.		Refractive Index.	
°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Maumené. °C.	Observer.	Butyro-refractometer.	
15	0 9458	Hobein	203·8	Hobein	145·6	Hobein	0·93	Tortelli and Ruggeri	136·5[1]	Tortelli and Ruggeri	"Degrees" at 35° C.	Observer.
15·5	0·9395	Nash	210·4	Tortelli and Ruggeri	160·6	Tortelli and Ruggeri Nash					75	Tortelli and Ruggeri
15 (water 15° = 1)	0·9432	Tortelli and Ruggeri			160·7				Spec. Temp. React.		Refractive Index. At 23·5° C.	
27 (water 15° = 1)	0·9370	,,							267	Tortelli and Ruggeri	1·4825	Nash
100 (water 15° = 1)	0·8737	,,										

[1] Jean's thermelæometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
94·4	Tortelli and Ruggeri	12·2 (Titer test)	Tortelli and Ruggeri	14·5	Tortelli and Ruggeri	214·2	Tortelli and Ruggeri	161·9	Tortelli and Ruggeri
						206·3	Lewkowitsch	181·8	Lewkowitsch
						210·5 (Saponification value)	,,	165·0	Nash
								Liquid Fatty Acids.	
								178·1	Tortelli and Ruggeri
								191·1	Lewkowitsch

WHITE ACACIA OIL [1]

French—*Huile d'acacia blanc.* German—*Weiss-Akazienöl.*
Italian—*Olio di acacia bianca.*

This oil has been obtained from the seeds of the white acacia, *Robinia pseudoacacia*, L., cultivated in South Russia. On extraction with petroleum ether the seeds yielded 13·3 per cent of oil.

Physical and Chemical Characteristics of White Acacia Oil

Saponification Value.	Iodine Value.	Reichert-Meissl Value.
192·4	161·0	1·2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Neutralisation Number.	Mean Molecular Weight.	Iodine Value.
94·32	200·1	280·4	160·7

The specimen examined by *Jones* contained 0·20 per cent of unsaponifiable matter. The oil possesses strong drying power, as is indicated by its high iodine value. From the total mixed fatty acids, 3·7 per cent of solid fatty acids were obtained; amongst these were identified stearic and erucic acids. The liquid fatty acids consist of oleic, linolic, and linolenic acids, linolic acid predominating. The oil is easily oxidised on exposure to the air.

CEDAR NUT OIL

French—*Huile de noix de cèdre.* German—*Cedernussöl, Zirbelkieferöl.*
Italian—*Olio di noce di cedro.*

For tables of characteristics see p. 73.

Cedar nut oil is obtained from the nuts of the Siberian cedar or stone pine (*Pinus cembra*, L.), a tree forming large forests in Southern Siberia and occurring largely in the Alps and the Carpathians. The oil belongs to the fir seed oils, but on account of its very high iodine value as compared with the iodine values of the other fir seed oils, it is preferable to describe it separately.

[1] Valentin Jones, *Mittheil. k. k. technolog. Gewerbe-Museum*, 1903, 223.

Physical and Chemical Characteristics of Cedar Nut Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.
0	0·932	Kryloff[1]	− 20	Kryloff	191·8	Kryloff	149·5-150·5	Kryloff	2·0	Kryloff	98[3]	v. Schmoelling
15	0·930	v. Schmoelling[2]			191·8	v. Schmoelling	159·2	v. Schmoelling	3·77 per cent volatile acids	v. Schmoelling		

[1] *Journ. Soc. Chem. Ind.* 1899, 501. [2] *Chem. Zeit.* 1900, 815. [3] By Archbutt's method.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.	Observer.
Per cent.	Observer.	°C.	Mgrms. KOH.		Per cent.	
93·33	Kryloff	11·3	193	290	161·3	v. Schmoelling
91·97	v. Schmoelling				Liquid Fatty Acids.	
					184	

The oil has a golden-yellow colour and a pleasant taste. It is soluble with difficulty in cold carbon bisulphide and in cold benzine, but dissolves easily on warming.

Amongst the solid acids, palmitic acid was identified; the liquid fatty acids consist chiefly of linolic acid. Oleic and linolenic acids are present in small quantities only. The unsaponifiable matter in the specimen examined by *v. Schmoelling* was 1·3 per cent; the acetyl value of the fatty acids *after six days' standing* was 81·9.

The oil is used in Siberia for edible purposes.

GARDEN ROCKET OIL[1]—DAME'S VIOLET OIL

French—*Huile de julienne.* German—*Rothrepsöl.*
Italian—*Olio di Hesperide.*

For tables of characteristics see p. 75.

This oil is expressed from the seeds of the garden rocket, *Hesperis matronalis*, L. The seeds contain approximately 30 per cent of oil. When freshly expressed the oil is of green colour, becoming brownish on keeping. It is odourless, and possesses a somewhat bitter taste.

Garden rocket oil is expressed in France and Switzerland, and is used as a burning oil.

[1] De Negri and Fabris, *Annali del Laborat. Chim. delle Gabelle*, 1891-92, 151.

Physical and Chemical Characteristics of Garden Rocket Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9282	Schübler	– 22 to – 23	Schübler	191·8	De Negri and Fabris	154·9-155·3	De Negri and Fabris	125-127·5	De Negri and Fabris
0·9315	Villon								
0·9335	De Negri and Fabris								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.	Observer.
°C.	°C.	Per cent.	
16-14	20-22	157	De Negri and Fabris

HEMP SEED OIL

French—*Huile de chènevis.* German—*Hanföl.*
Italian—*Olio di canapa.*

For tables of characteristics see p. 77.

Hemp seed oil is obtained from the seeds of the hemp plant, *Cannabis sativa*, L. The seeds yield about 30 per cent of oil. The hemp plant is cultivated in France, Belgium, Germany, Northern Italy, Algeria, North America, India, and Japan. The quantities of hemp seed produced in France are given in the following table :—

Cultivation and Production of Hemp Seed in France

Year.	Hectares under Cultivation.	Kilograms.
1897	32,863	9,507,700
1898	29,250	8,810,400
1899	29,032	8,502,300
1900	26,790	8,598,800
1901	25,760	7,976,800
1902	24,374	4,918,500
1903	22,670	9,146,000
1904	20,774	9,563,700

The colour of the freshly expressed oil is light green to greenish-yellow, becoming brownish-yellow on keeping. The solid glycerides in hemp seed oil are stated to consist of stearin and palmitin ; but it is very likely that stearin is absent. The liquid fatty acids in hemp seed oil are, according to the researches of *Bauer*, *Hazura*, and *Grüssner*, linolic acid and smaller quantities of oleic, linolenic, and isolinolenic acids.

Pure hemp seed oil may be easily identified by its high iodine absorption.

Hemp seed oil is used as a paint oil, though less frequently in this country than on the Continent. Considerable quantities are employed (on the Continent) for making soft soaps, which are characterised by a dark-green colour. The lower qualities of hemp seed oil are stated to be used in the manufacture of varnishes.[1]

Hemp seed oil is also produced in Manchuria ; but owing to the fact that the seed is grown—and harvested—together with other (wild) seed, which yields about 16 per cent of a non-drying oil, the Manchurian oil is of very low quality as regards drying powers.

[1] Lidoff, *Chem. Revue*, 1900, 120.

Physical and Chemical Characteristics of Hemp Seed Oil

Specific Gravity.		Solidifying Point.	Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·925-0·931	Allen	Thickens at −15 and solidifies at −27	193·1	Valenta	157·5	Benedikt	98	Maumené	+30 to +34	Jean
0·9270	Chateau		192·8	De Negri and Fabris	140·5	De Negri and Fabris	95-96	De Negri and Fabris	+34 to +37·5 at 22° C.	Pearmain
0·9255	Massie									
0·9280	De Negri and Fabris		190-191·1	Lewkowitsch	148	Lewkowitsch				
					159-166	Shukoff[1]				

[1] Russian oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
15	Hübl	19	Hübl	122·2-125·2	Morawski and Demski
16	De Negri and Fabris	18-19	De Negri and Fabris	141	De Negri and Fabris
14-15		17-18			
Titer Test.					
15·6-16·6	Lewkowitsch				

BUCK-THORN OIL [1]

French—*Huile de nerprun.* German—*Kreuzdornöl, Purgierwegdornöl.*
Italian—*Olio di spina cervina, Olio di ramno cattartico.*

Physical and Chemical Characteristics of Buck-thorn Oil

Specific Gravity.		Reichert-Meissl Value.	Iodine Value.
At ° C.		c.c. $\frac{1}{10}$ norm. KOH.	Per cent.
15 (water of 4° = 1)	0·9195 (?)	0·89	155

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.
Per cent.		Per cent.	
95·77	288·9	160·6	25·8

This oil was prepared by extracting the seeds obtained from the berries of the purging buck-thorn, *Rhamnus cathartica*, L., with ether. The oil thus obtained had an acid value of 5·64 and contained 0·59 per cent of unsaponifiable matter, of which 0·48 per cent consisted of phytosterol and 0·11 per cent of a hydrocarbon, melting at 81-82° C. and belonging to the ethane series. A detailed examination of the fatty acids gave the following result :—

Volatile fatty acids	0·24 per cent.
Stearic acid	6·00 ,,
Palmitic acid	1·12 ,,
Oleic acid	30·10 ,,
Linolic acid	35·2 ,,
Linolenic acid and isolinolenic acids	22·4 ,,

The low specific gravity of the oil would hardly appear to correspond to this composition.

[1] N. Krassowski, *Journ. russ. phys.-chem. Ges.* 1905, xxxviii. 144-61.

BURDOCK OIL—BUR OIL

French—*Huile de bardane.* German—*Klettensamenöl.*
Italian—*Olio di bardana.*

This oil[1] is obtained from the seeds of *Lappa minor*, D. C. (*Arctium Lappa*, L.). The seeds are of the size of linseed, but have a more spherical form. One litre of seeds obtained from the Charkoff district[2] weighed 641 grams. They consisted of 46·4 per cent of husks and 53·6 per cent of "meats." The total seeds contained 14·8 per cent of oil.

The pressed oil is pale yellow. It has an odour resembling that of linseed oil, and a somewhat bitter taste. The specific gravity of the oil at 17° C. is 0·9255; its saponification value, 196·6; its iodine value, 153·6; and its *Reichert-Meissl* value, 0·95. The iodine value of the insoluble fatty acids is 162. The acid value of the specimen examined by *Lidoff*[2] was 2·0.

GYNOCARDIA OIL[3]

French—*Huile de gynocardia.* German—*Gynocardiaöl.*
Italian—*Olio di gynocardia.*

For tables of characteristics see p. 80.

This oil is obtained from the seeds of *Gynocardia odorata*, R. Br. Up to the year 1900 chaulmoogra oil was generally believed to be derived from the seeds of *Gynocardia odorata*. Hence in the earlier literature gynocardia oil was described as identical with chaulmoogra oil, until *Power*, by a close investigation of the oils derived from the chaulmoogra family, and of the oil procured from genuine seeds of *Gynocardia odorata*, firmly established the characteristics of each individual oil. *Gynocardia odorata* is a native of Sikkim, Assam, and Chittagong in Bengal. In Assam the oil is sometimes expressed by the natives.

The shells form 37 per cent of the total weight of the seeds. The kernels furnish by expression fatty oil equivalent to 19·5 per cent of the entire seed. By extracting the total powdered seed with ether the amount of oil was raised to 27·2 per cent.

Gynocardia oil is, at the ordinary temperature, a light yellow liquid, resembling linseed oil in its odour. In contradistinction to the oils belonging to the chaulmoogra family, it is optically inactive.

[1] The production of this oil, as also of poppy, nettle, and mallow seeds, by "expression," was claimed by English patent 711, 1717 (T. Smith).

[2] A. P. Lidoff, *Chem. Zeit.* 1904, Rep. 161.

[3] Power and Barrowcliff, *Journ. Chem. Soc.* 1905, 896.

The acid value of the expressed oil was 4·9, and of the extracted oil 5·0. The unsaponifiable matter was identified as phytosterol. The mixed fatty acids contained very small proportions of volatile acids, amongst which formic and acetic acids were recognised. Amongst the insoluble acids were found palmitic acid, oleic acid, linolenic acid, and isolinolenic acid. The last three acids were identified by means of their oxidation products, viz. dihydroxystearic acid, tetrahydroxystearic acid, and isolinusic acid respectively.

Gynocardia oil is a good drying oil.

Physical and Chemical Characteristics of Gynocardia Oil

	Specific Gravity.		Saponification Value. Mgrms. KOH.	Iodine Value. Per Cent.
	At ° C.			
Expressed oil . .	25°	0·925	197·0	152·8
Extracted oil . .	25°	0·927	199·6	152·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Neutralisation Value. Mgrms. KOH.	Iodine Value. Per cent.
199·8	162·6

NSA-SANA OIL

This oil was prepared in the *Imperial Institute*[1] by extracting Nsa-sana seeds from West Africa. These seeds are believed to be derived from a species of *Aleurites*, *Ricinodendron africanum*. The following characteristics were ascertained :—

Specific gravity at 20° C.	0·9320
Saponification value	191·6
Iodine value	147·7
Insoluble fatty acids + unsaponifiable . .	95·20 per cent.
Titer test of fatty acids	35·7° C.

The oil dries on exposure to the air at the ordinary temperature in one day and leaves a wax-like residue. The expressed cake is unsuitable for cattle food probably owing to the presence of an alkaloid.

[1] *Bull. Imp. Inst.* 1907, 369.

WALNUT OIL—NUT OIL

French—*Huile de noix.* German—*Nussöl, Wallnussöl.*
Italian—*Olio di noce.*

For tables of characteristics see pp. 82, 83.

This oil is obtained from the seeds of the common walnut tree, *Juglans regia*, L. The fruit intended for the preparation of the oil must be allowed to ripen fully and be kept two to three months before being pressed, as fresh seeds yield a very turbid oil, difficult to clarify. The kernels contain from 63 to 65 per cent of oil. The cold-drawn oil is almost colourless, or of a pale yellowish-green tint, and has a pleasant smell and an agreeable nutty taste; the hot-pressed oil has a greenish tint and an acrid taste and smell.

The solid glycerides of walnut oil are stated to contain myristic and lauric acids; the liquid fatty acids of the oil consist chiefly of linolic acid, and of smaller quantities of oleic, linolenic (and isolinolenic ?) acids. *Hehner* and *Mitchell* obtained from 1·42 to 1·9 per cent ether-insoluble brominated glycerides in the bromide test. The statement made by *Kebler*[1] that a sample of walnut oil had the *Reichert-Meissl* value 15, requires confirmation; all the more so as the saponification value of the sample was found to be 190·1 to 190·5.

One part of walnut oil dissolves in 188 parts of cold, or in about 60 parts of boiling alcohol. On cooling, crystals separate from the solution.

Walnut oil has good drying powers. Its comparatively high price acts as an incentive to adulterate it with linseed oil. The latter is detected by a higher *iodine value* than the normal one, and by a higher yield of ether-insoluble brominated glycerides (or acids) than 2 per cent.[2] The presence of *cotton seed* oil, *sesamé* oil, and *arachis* oil is recognised by a low iodine absorption. Confirmation is obtained in the case of the two first-named oils by their characteristic colour reactions, and in the case of arachis oil by the arachidic acid test. Walnut oil, in its turn, is used as an adulterant for olive oil, its higher iodine absorption being "corrected" by the addition of lard oil.

The best qualities of walnut oil are almost colourless; such oil is therefore preferred to any other for the making of white paints for artists. These paints are less liable to crack than the paints made with linseed oil. Poppy seed oil, which is also used in the preparation of white paints for artists, is differentiated from walnut oil by not yielding ether-insoluble brominated glycerides. Walnut oil containing notable amounts of free fatty acids is unsuitable for making paints; such oil finds an outlet in the manufacture of soft soaps.

[1] *Amer. Journ. Pharm.* 1901, 73, 173.

[2] Halphen's method (*Bull. Soc. Chem.* 1905 (35), 571), viz. to add to the sample bromine in carbon-tetrachloride solution, is a modification of the bromide test (Vol. I. Chap. VIII.). Being a qualitative test, small amounts of linseed oil would escape detection.

Physical and Chemical Characteristics of Walnut Oil

Specific Gravity.			Solidifying Point.	Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.				Viscosity in Redwood's Viscosimeter.	
At °C.		Observer.	°C.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.		Observer.			Seconds at 70° F.	Observer.
12	0·928	Saussure	Thickens at −12 and solidifies at −27·5	196·0	Valenta	143	Hübl	0·00	Crossley and Le Sueur	101	Maumené	1·4804	Blasdale			231·8	Crossley and Le Sueur
15	0·925-0·926	Allen		188·7	Dieterich	147·9-151·7	Dieterich			96	De Negri and Fabris						
15	0·9265	De Negri and Fabris		194·4	Maben	145·7	Hazura					Oleo-refractometer.					
				193·81-197·32	De Negri and Fabris	147·92-148·4	Petkow [2]			110	Blasdale						
15	0·9256	Blasdale [1]				143·3	Peters					"Degrees."	Observer.				
15·5	0·9259	Crossley and Le Sueur		194·4	Blasdale	144·5-145·1	De Negri and Fabris										
(water 15·5 = 1)				192·5	Crossley and Le Sueur	132·1	Blasdale					+35 to +36	Jean				
25	0·919	Saussure				143·1	Crossley and Le Sueur					Butyro-refractometer.					
94	0·871	,,										At °C.		Observer.			
												40	64·8	Crossley and Le Sueur			
												40	67-68	Petkow [2]			

[1] Blasdale (*Journ. Soc. Chem. Ind.* 1896, 206). Oil from *Juglans regia* grown in California.

[2] Five samples of cold-pressed oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
95·4	Crossley and Le Sueur.	16	Hübl	20	Hübl	150·05	De Negri and Fabris
				16-18	De Negri and Fabris	Liquid Fatty Acids	
				15	Blasdale	167	Tortelli and Ruggeri.

Bellier[1] bases the detection of poppy seed oil in walnut oil on the different solubilities of their mixed fatty acids in 70 per cent alcohol at 17°-19° C. in the presence of a definite amount of potassium acetate. Poppy seed oil contains more solid fatty acids than walnut oil, and gives a more abundant precipitate. The test is made as follows:— 1 c.c. of the oil is warmed with 5 c.c. of a solution of alcoholic potash, containing 16 grms. in 100 c.c. of 92 per cent alcohol, until a clear solution is obtained. The test-tube is corked and warmed in a water bath for half an hour to 70° C. Then so much of a 25 per cent solution of acetic acid is run in as is required to neutralise exactly the 5 c.c. of alcoholic potash solution (this must be ascertained in a blank test). The test-tube is then corked and placed in water of 25° C., and finally in water of 17°-19° C., and shaken frequently. Pure walnut oil gives only a minute precipitate, which hardly covers the bottom of the test-tube, whereas poppy seed oil yields a copious precipitate.

Balavoine[2] has tested this method, and finds that only from 20 per cent upwards of poppy seed oil can thus be detected in walnut oil. Moreover, rancid oils seem to give a more copious precipitate, in even a shorter time, than neutral oils.

Bellier's method is not an exact one, and can only give rough indications when all other methods fail. *Bellier* proposed this method with a view to detecting also other vegetable oils, such as linseed oil, cotton seed oil, sesamé oil, rape oil, arachis oil, olive oil; but the methods given above will be found much more reliable.

[1] *Ann. chim. appliq.* 1905, 52.
[2] *Journ. Suisse de Chimie et Pharmacie*, 1906, 15.

ARBUTUS UNEDO OIL[1]—ARBUTE SEED OIL

French—*Huile d'Arbouse.* German—*Sandbeerenöl.* Italian—*Olio di Corbezzola.*

The fruits of *Arbutus unedo* are used (near Perugia) for the commercial production of alcohol. The fatty oil existing in the seeds to the extent of 39·03 per cent is retained in the still residue. The insoluble fatty acids (including the unsaponifiable matter) amount to 92·5 per cent. They consist of palmitic, oleic, linoleic, and isolinoleic acids, the two latter predominating. The quantitative determinations carried out according to *Hazura's* method gave 3·43 per cent oleic acid, 53·75 per cent linolenic acid, and 24·33 per cent isolinolenic acid.

Physical and Chemical Characteristics of Arbutus Unedo Oil

Specific Gravity.		Solidifying Point.	Saponification Value.	Iodine Value.	Reichert-Wollny Value.	Maumené Test.	Butyro-refractometer.	
At °C.		°C.	Mgrms. KOH.	Per Cent.	c.c. $\frac{1}{10}$ KOH.	°C.	At °C.	"Degrees."
15	0·9208	- 27	208	147·8	0·86	103·5 (In Tortelli's apparatus, olive oil being used as a diluent.)	25	71

LINARIA OIL[2]

French—*Huile de linaire, Huile de lin sauvage.* German—*Leinkrautöl.* Italian—*Olio di linaria.*

This oil has been obtained from the seeds of *Linaria reticulata* (belonging to the *Antirrhineæ*), which contain 37·5 per cent of oil. *Fokin* states that the oil yields no linolic acid.

Physical and Chemical Characteristics of Linaria Seed Oil

Specific Gravity.		Saponification Value.	Iodine Value.
At °C.		Mgrms. KOH.	Per cent.
20 (water at 18° = 1)	0·9217	188·6	140·0

[1] G. Sani, *Atti R. Accad. dei Lincei*, Rome, 1905, xiv. [2] 619-623 ; *Chem. Centr.* 1906, i. 373.

[2] Fokin, *Chem. Revue*, 1906, 130.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids + Unsaponifiable.	Specific Gravity.	Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.	Acetyl Value.
Per cent.	At 19° C. (water 19° = 1).	°C.	°C.	Mgrms. KOH.	Per cent.	
94·1	0·903	13-8·5	14-22	201·1	148·5	12·3

SAFFLOWER OIL—SAFFRON OIL

French—*Huile de carthame.* German—*Safloröl.*
Italian—*Olio di cartamo.*

For tables of characteristics see pp. 88, 89.

For table of characteristics of Indian oils see p. 87.

Safflower oil is obtained from the seeds of *Carthamus tinctorius*, L., a plant until recently cultivated all over India for the preparation of the saffron dye. The chief localities where the plant is grown are Bengal, Hyderabad, Cawnpore, Bombay, and the Punjab. Two distinct varieties of the plant are grown, *Carthamus tinctorius* and *Carthamus oxyacantha.* The oil from *C. tinctorius* from Mombo (German East Africa) gave numbers which do not differ from those given below for the Indian seeds.[1]

The cultivation of the plant has also been extended to Egypt, the Caucasus, and Turkestan, and seems to be on the increase in these countries. The seeds contain from 30 to 32 per cent of oil, but owing to the thick husk, only 17 to 18 per cent of the oil are obtainable by pressing. The press cake contains, therefore, a large amount of woody fibre, as is shown by the following analysis of a pressed cake, prepared by the author on a semi-large scale :—

	Per cent.
Albuminoids	20·11
Oil	11·91
Starch, sugar, etc.	10·83
Woody fibre	40·75
Moisture	11·60
Ash	4·80

This analysis points to the necessity of first decorticating the seeds, so as to lay bare the kernel which forms 40 per cent of the seed. Special machinery is required for this purpose, the ordinary Anglo-American rollers having been found unsuitable on account of the

[1] Fendler *Chem. Zeit.* 1904 No. 74

extreme hardness of the husk. An experiment carried out on a semi-large scale [1] with a special machine yielded over 31 per cent of kernels ("meats").

The oil is prepared in India on a small scale from two kinds of fruits—the cultivated white and glossy form, and the small fruit of a mottled brown, grey, or white appearance. The oil obtained from the cultivated variety by expression in the cold is pale yellow; it has a pleasant taste simulating that of sunflower oil, so that it can be largely used for edible purposes. Considerable quantities are pressed in India together with other seeds, especially arachis nuts.

The saturated fatty acids contained in safflower oil consist of palmitic and stearic acids, as ascertained by fractional precipitation with magnesium acetate of those acids which yield lead salts insoluble in ether. The high iodine value of the oil points to large amounts of unsaturated acids. *Le Sueur*,[2] examining the oil by the oxidation and bromination methods, states that the liquid fatty acids consist of oleic and linolic acids; no evidence of the presence of linolenic acids was obtained. *Walker* and *Warburton*, however, ascertained in the author's laboratory [3] that whilst the oil yields no ether-insoluble brominated glycerides, the fatty acids give from 0·65 to 1·65 per cent of ether-insoluble bromides. *Tylaikoff* confirms the presence of oleic and linolenic acids, he having obtained the oxidation products of these two acids; the same observer proved also the occurrence of linolic acid by isolating tetrabromostearic acid after brominating the acids. The unsaponifiable matter in several specimens of oil examined in my laboratory amounted to 1·5 per cent. The true acetyl value of several samples has been found to be 16·1, 12·85, and 12·78 (*Lewkowitsch*). In view of the importance this oil may acquire, a number of analyses, which have been summarised partly in the table of characteristics, may be added here.

[1] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.* 1903, 590.

[2] *Journ. Soc. Chem. Ind.* 1900, 104. [3] *Analyst*, 1902, 237.

Indian Safflower Oils (Crossley and Le Sueur [1])

Name.	Description.	Source.	Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Fatty Acids + Unsaponifiable.	Refraction at 40° C.	Viscosity.		Acid Value.	Optical Activity in 200 mm. tube.
								Butyro-refracto-meter.	Seconds at 70° F.	Compared with Water.		
								"Degrees"				
Carthamus tinctorius	...	C. Provinces	0·9267	192·50	140·05	...	95·30	65·2	256·1	10·08	10·41	+8′
,, ,,	Pressed oil	Bengal	0·9264	193·30	144·40	...	...	...	247·8	9·76	3·68	+7′
,, ,,	...	Punjab	0·9275	186·60	138·64	0·00	...	...	274·5	10·81	8·28	...
,, ,,	From cultivated form	,,	0·9267	189·60	144·05	...	...	...	249·1	9·81	0·76	+10′
,, ,,	From wild form	,,	0·9253	187·40	129·80	...	...	...	...	...	2·90	+12′
,, ,,	By cold dry expression	Hyderabad	0·9277	187·90	138·60	...	...	...	274·7	10·79	2·58	+14′
,, ,,	From dye plant	Bombay	0·9262	187·20	143·40	...	...	65·2	250·3	9·85	2·67	+8′
,, ,,	From oil seed plant	,,	0·9269	191·30	149·93	0·00	...	...	249·6	9·83	6·20	+4′
,, ,,	Var.: Thornless	Cawnpore	0·9271	189·40	141·42	0·00	...	...	258·8	10·19	5·92	+7′
,, ,,	Var.: Thorny	,,	0·9251	190·52	141·12	...	...	...	243·0	9·57	20·02	...
,, ,,	...	Madras	0·9280	192·42	142·85	...	...	...	268·8	10·58	4·12	+6′
,, oxyacantha	...	Punjab	0·9270	189·40	135·49	...	95·44	...	294·0	11·57	3·66	+7′

[1] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Characteristics of Safflower Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.		Viscosity in Redwood's Viscosimeter.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 16°C.	Observer.	Seconds at 70° F.	Observer.
15·5 (water at 15·5° C. = 1)	0·9251-0·9280	Crossley and Le Sueur	Becomes turbid at −13°, not completely solidified at −18°	Fendler	186·6-193·3	Crossley and Le Sueur	129·8-149·9	Crossley and Le Sueur	0·0	Crossley and Le Sueur	1·477	Tylaikoff	249·1-294	Crossley and Le Sueur
,,	0·9274	Lewkowitsch			192·2	Lewkowitsch	146·5	Lewkowitsch	1·45-1·63	Jones			235	Lewkowitsch
,,	0·9246	,,			190·0	,,	147·3	,,	0·69-0·88	Tylaikoff	Butyro-refractometer at 40° C.			
,,	0·9250	Tylaikoff			194	Tylaikoff	143-144·5	Jones [1]			65·2	Crossley and Le Sueur		
20	0·9277	Jones [1]			194·4	Jones [1]	127·9	Fabris [2] and Settimj						

[1] *Chem. Zeitg.* 1900, 272.

[2] *Atti del VI Cong. internaz. di chimica applic.* (Settimj, Roma, 1907, vol. v. 750). The seeds examined yielded by extraction with ether 25 per cent of oil which gave 90 per cent of liquid fatty acids.

Physical and Chemical Characteristics of the Insoluble Fatty Acids.

Insoluble Acids +Unsaponifiable.		Specific Gravity.		Solidifying Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
95·4	Crossley and Le Sueur	0·9135	Fendler	16 (Titer Test)	Lewkowitsch	199	Fendler	148·2 132·5	Fendler F. and S.
				Melting Point.		Liquid Fatty Acids.			
				16-16·5	Fabris and Settimj	191·4	Fendler	159·6 150·8 140·5	Lewkowitsch Fendler F. and S.

Safflower oil has good drying powers, and although it cannot replace linseed oil in all its applications, it should certainly form a substitute for it in many instances, and find extended use in the manufacture of soft soap. In *Livache's* test the oil absorbed 6·4 per cent of oxygen after two days (*Tylaikoff*).

Safflower oil is heated by the natives to obtain an oil suitable for the preservation of leather vessels, ropes, etc., exposed to the action of water. A specimen of oil thus prepared had the specific gravity 0·9634, the saponification value 188·0, and the iodine value 128·9. It therefore represents a kind of "boiled oil." The special process of preparing this "boiled oil" is carried out in India as follows:— The seeds of the wild safflower, *Carthamus oxyacantha*, are expressed in the hot, and the oil is boiled in earthenware vessels for twelve hours, during which time considerable quantities of acroleïn volatilise. The "boiled" oil is immediately placed in flat dishes, partly filled with cold water, so that the oil solidifies to a jelly-like thick mass termed "roghan" (Afridi wax). This "boiled oil" is employed by the natives in Lahore, Delhi, Bombay, and Calcutta for the manufacture of "Afridi wax linoleum." It is also used by the natives for drawing artistic designs on woven cloth, the production of which was considered for a long time a valuable secret. The pattern is made by the natives by means of finely pointed staves dipped in the "roghan," which is drawn in very fine threads, and so deposited on the cloth. When completely dry, it forms an indelible pattern.

Considerable quantities of safflower oil are used as a burning oil, notably in Egypt.

KAYA OIL[1]

French—*Huile de Kaya.* German—*Kayaöl.*
Italian—*Olio di Kaya.*

This oil is obtained from the seeds of *Torreya nucifera*, S. and Z. (*Taxaceæ*), a plant growing wild in the mountainous regions in several districts of Japan. The seeds are of long oval shape with pointed ends; they are 1·5 to 2·5 cm. long, and weigh on an average 1 gram. The black-coloured husks are very hard, and enclose a pale yellow kernel covered with a reddish-brown skin. The seeds consist of 32 per cent of husks and 68 per cent of kernels. The following numbers were obtained on analysing various specimens of the kernels:—Moisture, 2·67 to 5·04 per cent; oil, 51·07 to 51·70 per cent; ash, 2·20 to 2·29 per cent.

The oil is prepared commercially by steaming and pressing the comminuted seeds whereby about 13 per cent of oil (by volume) are obtained. Cold-pressed oil is pale yellow, and has a faint odour and a mild taste. Commercial oils are yellow and have a faint resinous odour.

The following characteristics were obtained in the examination of one cold-pressed and two specimens of commercial oils:—

	Cold-pressed Oil.	Commercial Oils.	
		I.	II.
Oil—			
Specific gravity at 15° C.	0·9238	0·9233	0·9244
Saponification value	188·4	188·3	188·0
Iodine value	142·2	138·0	133·4
Reichert-Meissl value	0·93	...	...
Refractive index at 20° C.	1·477	1·4760	1·4757
Fatty Acids—			
Insoluble acids + unsaponifiable	95·7%	...	...
Specific gravity at 98° C.	0·8509	..	...
Neutralisation value	192·81	...	...
Mean molecular weight	290·96	...	...
Iodine value	149·5	...	...

The acid values of the three specimens were 1·5, 4·2, and 12·7 respectively.

The insoluble fatty acids deposited at the ordinary temperature some crystals, which melted into the oily part at 25° C. In the elaïdin test no solidification was observed after two hours; at the end of twenty-four hours only a small deposit of buttery consistence was found. When the oil is heated in a thin layer at 100° C. for three hours it dries to an elastic film. A "boiled" oil prepared by heating

[1] Tsujimoto, *Journ. Coll. Engin. Tokyo*, 1908, 83.

with manganese borate or resinate dries completely after twenty-four hours at the ordinary temperature.

In the bromide test no ether insoluble hexabromide was found; there was, however, obtained by *Kametaka* a tetrabromide, of melting point 114° C. Hence the presence of linolic acid is proved.

The "cold-drawn" kaya oil is consumed as an edible oil; the commercial qualities are used for burning, in the manufacture of papers, and as an insecticide.

INUKAYA OIL (BÉBÉ OIL)[1]

French—*Huile d'inukaya.* German—*Inukayaöl.*
Italian—*Olio di inukaya.*

This oil is obtained from the seeds of the inukaya tree *Cephalotaxus drupacea*, S. and Z., an evergreen plant belonging to the family of *Taxaceæ*. The seeds of the inukaya tree are of small ellipsoidical shape; they weigh on an average 0·59 grm., and consist of 33 per cent of brown husks and 67 per cent of light brown kernels having a resinous odour. The kernels gave the following numbers:—Moisture, 4·57 per cent; oil, 67·1 per cent; ash, 2·2 per cent. The oil (called "*bébé*" in the Shiga and Fukui districts) is prepared by steaming and pressing the powdered seeds; it is chiefly manufactured in the northern parts of the Shiga prefecture.

The "cold-drawn" oil prepared in the laboratory was a light yellow oil of slightly resinous odour, which did not solidify at − 15° C. The following characteristics were determined:—

Specific gravity at 15° C.	0·9250
Saponification value	188·5
Iodine value	130·3
Refractive index at 20° C.	1·476

Inukaya oil resembles kaya oil in many of its properties, but it dries less readily than the latter.

On account of its resinous odour the oil cannot be used as an edible oil. It is employed in the same manner as commercial kaya oil.

ECHINOPS OIL (THISTLE SEED OIL)

French—*Huile de chardon.* German—*Echinopsöl.*
Italian—*Olio di echinops.*

This oil is obtained from the seeds of *Echinops ritro*, D.C., a plant belonging to the family of *Compositæ*, and indigenous to Asia and the Mediterranean; the yield of oil from the seeds is 27·5 per cent.

[1] Tsujimoto, *Journ. Coll. Engin. Tokyo*, 1908, 85.

The characteristics found by *Wijs*[1] on examining two specimens of the oil, containing 4·4 per cent and 7·3 per cent of free fatty acids respectively, are given in the following tables.

The oil absorbs 9 per cent of oxygen (*Weger's* method). 1000 c.c. of absolute alcohol at 15° C. dissolve 51 grms. of the neutral oil (freed from fatty acids). The acetyl value of one specimen was 26·5.

The oil gives neither the *Halphen* nor the *Baudouin* reaction.

Physical and Chemical Characteristics of Echinops Oil

Specific Gravity.	Saponification Value.	Iodine Value.
At 20° C. (Water 4° = 1).	Mgrms. KOH.	Per cent.
0·9285-0·9253	189·2-190	138·1-141·2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
° C.	Mgrms. KOH.		Per cent.
11-12	192·3-192·9	291-292	139·1-143·8

POPPY SEED OIL

French—*Huile d'œillette, Huile de pavot.* German—*Mohnöl.* Italian—*Olio di papavero*

For tables of characteristics see pp. 95, 96.

Poppy seed oil is obtained from the seeds of the two varieties of poppy, *Papaver somniferum*, L., *P. album* and *P. nigrum*, D.C., by pressing. The plant is grown extensively in Asia Minor, Persia, India, Egypt, South Russia, and the North of France; the seeds yield from 45-50 per cent of oil.

Poppy seed is also produced in Manchuria, but owing to the fact that it is grown—and harvested—together with other wild seeds which yield about 16 per cent of a non-drying oil, the Manchurian oil is of very low quality as regards drying powers.

In France a distinction is made between *huile d'œillette* and *huile de pavot*. The former is obtained from indigenous, or at any rate European, poppy seed, whilst the name *huile de pavot* is given to the oil obtained from oversea seed. Since, however, by far the greatest

[1] *Zeit. f. Nahrungs- und Genussm.* 1903, 492.

part of expressed oils, both of European as also of oversea origin, is used as a table oil, all edible poppy seed oils are termed *huile d'œillette*. The following table makes, therefore, a distinction between "poppy seed *œillette*," *i.e.* European poppy seed, and "poppy seed *pavot*."

By far the largest quantities of poppy seed oil are crushed in France, both in the south (Marseilles) and in the north, and in Germany. The importance which this industry has reached may be gathered from the following figures:—

Year.	Poppy Seed *œillette*.		Poppy Seed *pavot*.		
	French Production.	Import into France.	Import into France.	Import into Marseilles.	Import into Germany.[1]
	Kilograms.	Kilograms.	Kilograms.	Kilograms.	Kilograms.
1896	8,646,800	95,100	23,482,600	7,112,500	20,540,600
1897	8,084,600	25,300	24,239,100	3,021,100	22,987,000
1898	8,146,500	26,700	17,815,400	2,908,500	25,371,000
1899	7,402,300	51,300	26,062,400	5,367,300	27,081,000
1900	6,201,300	58,300	21,912,900	2,973,500	28,749,000
1901	4,278,400	58,600	26,494,900	3,723,300	25,920,000
1902	6,226,900	12,600	28,310,000	5,047,200	31,140,000
1903	4,368,500	31,600	27,254,600	2,997,400	33,030,000
1904	6,160,300	11,200	35,249,400	6,101,600	33,610,000
1905	5,247,500	9,700	20,829,400	3,852,400	34,990,000
1906	5,676,400	14,100	26,507,500	3,481,500	28,961,100
1907	...	11,300	29,158,900	4,001,500	36,267,800

The chief countries of origin of the poppy seed pressed in Marseilles, are the Levant (Samsoun, Smyrna, Alexandrette) and India (Bombay, Calcutta). The Levant seeds are preferred to the Indian seeds, as they yield a finer oil (cp. "Sesamé Oil") and a larger proportion of it. The Levant seeds are white, grey, blue, or red, and yield on a large scale 39 to 40 per cent of oil. The Indian seed, which is mostly white and only rarely red, gives 36 to 38 per cent of oil in the oil mill.

The "cold-drawn" oil, the oil of the first pressing, is almost colourless or very pale golden yellow; this is the "white poppy seed oil" of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the "red poppy seed oil" of commerce.

Sweet (fine) table oil is prepared by cold expression in Marseilles and in the North of France (in Lille, Arras, Douay, Cambrai). The cold-pressed oil is filtered before being placed on the market. In some of these establishments paper filters are said to be used even at present.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

The cakes resulting as a by-product are rich in nitrogen and are fed to cattle; only when the cakes have become mouldy are they employed as a manure for early fruit.

[1] Mostly Indian seed.

In the following table the acid values of a number of commercial samples are recorded :—

Kind of Oil.	Free Fatty Acids calculated to Oleic Acid.	Observer.
	Per cent.	
	2·09	Rechenberg
	2·29	Salkowski
Salad oil, 26 samples	0·70-2·86	Nördlinger
Commercial oil, expressed, 5 samples	12·87-17·73	,,
Commercial oil, extracted, 5 samples	2·15-9·43	,,
East Indian oils, expressed, 4 samples	3·2-5·5	Crossley and Le Sueur[1]

The solid fatty acids in poppy seed oil have not yet been investigated; according to early statements, lauric and myristic acids are absent, whilst palmitic and stearic acids are said to be present. It is, however, most likely that palmitic acid is the only solid acid. According to *Tolman* and *Munson*[2] the proportion of solid fatty acids, as determined by the lead-salt-ether method, is 6·67 per cent of the total fatty acids. The liquid fatty acids in poppy seed oil were stated by *Hazura* and *Grüssner* to consist of 5 per cent of linolenic acid, 65 per cent of linolic acid, and about 30 per cent of oleic acid. Since, however, the liquid fatty acids from poppy seed oil yield practically no ether-insoluble bromides, the quantity of linolenic acid must be very small. According to a recent examination, by *Utz*,[3] of poppy seed oils, obtained by extracting the seed with petroleum ether, the iodine value lies much higher than has been found hitherto. In the following table I reproduce *Utz's* results :—

	Iodine Value.	Refractive Index. At 15° C.	Butyro-refractometer. "Degrees" at 15° C.
Indian poppy seed oil	153·48	1·4772	78·1
Levantine ,, ,,	157·52	1·4774	78·4
German ,, ,,	156·94	1·4774	78·4

The unsaponifiable matter in poppy seed oil amounts to about 0·5 per cent, and consists chiefly of phytosterol, with which is admixed some impurity that can only be separated from the phytosterol by repeated crystallisation. Thus the crude phytosterol had to be recrystallised eight times before crystals of the melting point 136-137° C. could be obtained. The crystals of phytosteryl acetate from poppy seed oil melted at 125·5-126° C. (*Bömer* and *Winter*).

[1] *Journ. Soc. Chem. Ind.* 1898, 991. [2] *Journ. Amer. Chem. Soc.* 1903, 690.
[3] *Chemiker Zeitung*, 1903, 1177 ; 1904, 257.

Physical and Chemical Characteristics of Poppy Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.			Viscosity.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
15	0·924	Souchère	−18	Girard	194·6	Valenta	136	Hübl	0·00[2]	Crossley and Le Sueur	86-88	Archbutt De Negri and Fabris	15	1·4773	Utz	253·9	Crossley and Le Sueur
,,	0·924-0·927	Allen			192·8	Moore	134	Moore			87-88·5		20	1·4751	Harvey	259·1	
,,	0·9262	Clarke			197·7	Dieterich	137·6-143·3	Dieterich					60	1·4586	Thoerner		
,,	0·924	Massie			193·6	De Negri and Fabris	139-141	Peters					Oleo-refractometer.				
,,	0·927	De Negri and Fabris			192-195	Oliveri	134-135	Souchère									
15·5 (water at 15·5=1)	0·9255-0·9268[2]	Crossley and Le Sueur			190·1	Lewkowitsch	136·8-137·6	De Negri and Fabris					"Degrees."		Observer.		
18	0·9245	Stilurell			193-194	Thoerner	133-138	Oliveri					+23·5 to +29 +35[1]		Jean		
98·99 (water at 15·5=1)	0·8738	Allen			189·0-196·8[2]	Crossley and Le Sueur	132·6-136	Lewkowitsch					+30 to +35 at 22° C.		Pearmain		
							134-135	Thoerner									
							133·7-137·1[2]	Crossley and Le Sueur									
							153·8-157·5	Utz					Butyro-refractometer.				
													At °C.		Observer.		
													15	78·3	Utz		
													25	74·5	Mansfeld		
														72	Beckurts and Seiler		
													40	63·4[2]	Crossley and Le Sueur		

[1] Very old sample.

[2] East Indian oils from the Punjab, Bengal, and the N.W. Provinces.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At 100° C. Water at 100° = 1.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·38	Dietzell and Kressner	0·8886	Archbutt	16·5	Hübl	20·5	Hübl	199	Thoerner	139	De Negri and Fabris	1·4506	Thoerner
				16·5	Thoerner	20-21	De Negri and Fabris						
94·97[1]	Crossley and Le Sueur					20·5	Thoerner			116·3 (?)	Thoerner		
				Titer Test.						Liquid Fatty Acids.			
				15·4-16·2	Lewkowitsch					149·6	Tortelli and Ruggeri		

[1] East Indian oils from the Punjab, Bengal, and the N.W. Provinces.

Poppy seed oil is, as a rule, contaminated with small quantities of sesamé oil, owing to the seed being usually expressed in the same works where sesamé oil is produced. Edible poppy seed oil is at present frequently adulterated with sesamé oil [1] and also with hazelnut oil, to improve the taste of edible oil obtained from stored seed. Both adulterants are detected by the lower *iodine absorption* of the sample; the presence of sesamé oil is ascertained by the characteristic *Baudouin* colour reaction (cp. "Sesamé Oil," p. 176).

The differentiation of poppy seed oil from walnut oil is of importance in the examination of white paints. The readiest means for this purpose is furnished by the bromide test; walnut oil yields from 1·4 to 1·9 per cent of ether-insoluble brominated glycerides, whereas poppy seed oil yields none. Poppy seed contains a larger proportion of solid acids [2] than walnut oil. (With regard to *Bellier's* method, cp. p. 83.)

Poppy seed oil is in its turn fraudulently added to olive oil (cp. p. 297); the high iodine value (unless masked by the addition of lard oil), in conjunction with a comparatively high specific gravity, indicate the adulteration. It is also used to adulterate peach kernel oil (*Bennett* [3]).

Mixtures consisting of 80 parts of poppy seed oil and 20 parts of beeswax are sold as fixing agents for artists' paints. A compound consisting of 100 parts of egg yolk and 75 parts of poppy seed oil (used for the same purpose) has been patented by *K. Lupus*.[4]

The best qualities of oil are used for edible purposes, and also for the preparation of the finest paints for artists. A mixture of equal volumes of "sun-bleached" poppy seed oil and bleached poppy seed "boiled" oil is extensively used for white pigments (*Lotter* [5]). A solution of fused gum mastic and Japan wax in poppy seed oil is known in commerce as "wax oil." On account of the high price of poppy seed oil only the lowest qualities can be employed for making soft soaps.

ASPARAGUS SEED OIL [6]

French—*Huile d'asperge.* German—*Spargelsamenöl.*
Italian—*Olio di asparaghi.*

Asparagus seed (*Asparagus officinalis*, L.) contains 15·3 per cent of a fatty oil of yellowish colour.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Butyro-refractometer. "Degrees" at 25° C.
0·928	194·1	137·1	75

[1] *Chemiker Zeitung*, 1903, 1177; 1904, 257.
[2] Bellier, *Ann. Chim. analyt. appl.* 1905, 52; *Analyst*, 1905, 132; *Chem. Centralbl.* 1905, 965 (cp. Schlegel, *Chem. Zeit.* 1904, 573); *Journ. Soc. Chem. Ind.* 1905, 459.
[3] *Chemist and Druggist*, 1908, 89.
[4] German patent 187,211, 1907.
[5] *Journ. Soc. Chem. Ind.* 1895, 168.
[6] W. Peters, *Archiv der Pharmacie*, 1902, 53.

On exposure to the atmosphere in a thin layer the oil dries to a hard varnish-like mass.

The glycerides in asparagus seed oil consist of palmitin, stearin, olein, and linolin. The presence of olein and linolin was proved by oxidising the liquid fatty acids, when dihydroxystearic acid and sativic acid were obtained. It is very likely that also linolenin and isolinolenin occur in the oil.

AMOORA OIL

French—*Huile d'Amoora.* German—*Amooraöl, Immergrünbaumöl.* Italian—*Olio di Amoora.*

Physical and Chemical Characteristics of Amoora Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.	Viscosity.	Insoluble Acids + Unsaponifiable.
At 15° C. (water at 15·5 = 1).	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refractometer. At 40° C. "Degrees."	Number of Seconds. At 70° F.	Per cent.
0·9386	189·7	134·86	1·64	64·5	375·8	93·23

This oil is expressed in Bengal from the seeds of *Amoora Rohituka, Aphanamixis Rohituka*, Roxb., Pierre (Evergreen tree). It is a clear, reddish-brown oil, and has a slight odour, resembling that of linseed oil. The specimen examined by *Crossley* and *Le Sueur*[1] had the acid value 17·03. The insoluble acids and unsaponifiable amounted to 93·23 per cent.

The oil is used by the natives medicinally and also as a burning oil.

MANIHOT OIL[2]—CEARA RUBBER SEED OIL

French—*Huile de Manihot.* German—*Manihotöl.* Italian—*Olio di Manihot.*

For tables of characteristics see p. 99.

This oil is obtained from the seeds of *Manihot Glaziovii*, Müll. Arg., a *Euphorbiacea* (from Lindi, East Africa), known as an india-rubber yielding tree.[3] This tree is indigenous to Ceara (Brazil); it is now being cultivated in East and West Africa. The seeds contain

[1] *Journ. Soc. Chem. Ind.* 1898, 991.

[2] Fendler and Kuhn, *Berichte d. deutsch. Pharmac. Gesellschaft*, 1905 (xv.), 426.

[3] According to Wildemann, *Le Caoutchuc et la Guttapercha*, 1906, iii. 455, there are several species of *Manihot Glaziovii*, of which two at least must be recognised as true species, viz. *Manihot ceara* and *Manihot Jequié*. These species of Manihot must not be confounded with *Manihot dulcis* (*M. utilissima*), the root of which yields tapioca.

25 per cent of kernels and 74·5 per cent of husks. The total seeds yield 9·94 per cent of oil, 8·98 per cent being furnished by the kernels and 0·96 per cent by the husks.

The oil is yellowish-green; its odour resembles that of olive oil. Its taste is slightly bitter. The specimen examined by *Fendler* and *Kuhn* had the acid value 2·18, and contained 0·9 per cent unsaponifiable matter.

In *Livache's* test the following numbers were found :—

Increase in Weight after	Per cent.
2 days	0·82
3 ,,	5·79
4 ,,	8·33
5 ,,	8·36
6 ,,	8·41
7 ,,	8·88

These figures notwithstanding, the oil when spread in a thin layer over a glass dried only after the lapse of a few weeks. At a temperature of 55° C., however, the drying was complete after ten hours.

The fatty acids contain about 10·97 per cent solid acids (of m.p. 54° C.) and 89·03 per cent (evidently found by difference) liquid fatty acids.

Physical and Chemical Characteristics of Manihot Oil

Specific Gravity at 15° C.	Solidifying Point.	Melting Point.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Refractive Index. Butyro-refracto-meter.	
	°C.	°C.			At °C.	"Degrees
0·9258	Turbid at 4	Below −17	188·6	137·0	40	62·9

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity at 25° C.	Solidifying Point. °C.	Melting Point. °C.	Neutralisation Number.	Saponification Number.	Iodine Value.
0·8984	20·5	23·5	197·6	200·1	143·1
					Liquid Fatty Acids.
					163·6

MELIA AZEDARACH OIL [1]

French—*Huile de Melia Azedarach.* German—*Meliaöl.*
Italian—*Olio di Melia.*

This oil is obtained from the seeds of *Melia Azedarach*, L. (Persian lilac; Bead tree; Laurier grec; Lilas des Indes; Sykomore [2]), which contain 39·36 per cent of oil. The total amount of oil obtainable from the fruits is 4·62 per cent. This oil must not be confounded with Margosa oil, the oil from *Melia Azadirachta*, L. (see "Vegetable Fats").

Specific Gravity at 15° C.	Solidifying Point. °C.	Melting Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer. "Degrees."
0·9235	-12°	-3	191·5	135·6	0·77	At 40° C. 65·1

Solidifying point of the fatty acids	19° C.
Melting point of the fatty acids	22° C.

As it would be very difficult to obtain the oil from the seeds on a commercial scale, it is hardly likely to acquire technical importance.

CROTON ELLIOTIANUS OIL [3]

This oil was obtained by extracting the seeds of *Croton Elliotianus.* It furnished the following characteristics:—

Specific gravity at 15° C.	0·9266
Saponification value	201·5
Iodine value	138·5
Insoluble acids + unsaponifiable	94 per cent
Titer Test	13·7° - 13·8° C.
The specimen had the acid value	4·24

The above numbers show that this oil differs considerably from the ordinary croton oil, which is derived from *Croton Tiglium*, L.

HENBANE SEED OIL [4]

French—*Huile de jusquiame.* German—*Bilsenkrautsamenöl.*
Italian—*Olio di giusquiamo.*

Henbane seed oil is obtained from the seeds of *Hyoscyamus niger*, L. The seeds yield about 35 per cent of oil.

[1] Fendler, *Apotheker Zeitung*, 1904, 55. [2] Watt, *Dictionary*, v. p. 223.
[3] *Bull. Imp. Institute*, 1907, 237. [4] Mjöen, *Journ. Soc. Chem. Ind.* 1897, 340.

The oil is yellow, slightly fluorescent, somewhat viscous, and dries readily.

Physical and Chemical Characteristics of Henbane Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert Value.	Insoluble Acids +Unsaponifiable.
				Per cent.
0·939	170·8	138	0·99	94·7

MILLET SEED OIL, see Appendix.

NIGER SEED OIL

French—*Huile de Niger* German—*Nigeröl.*
Italian—*Olio di Niger.*

For tables of characteristics see p. 102.

Niger seed oil is obtained from the seeds (more correctly *achenes*) of *Guizotia abyssinica* (L.), Cass. (*Guizotia oleifera*, D.C.), a plant indigenous to Abyssinia, and largely cultivated not only in East Africa, but also in the East and West Indies; it has also been grown as an experiment in Germany. The fruits are small, have a tooth-like shape, and are shining black in colour. The seeds contain from 40 to 45 per cent of oil. The oil (which first came into the English market in 1851) is yellow and has a nutty taste. Four specimens of East Indian oils examined by *Crossley* and *Le Sueur*[1] had acid values ranging from 5·21 to 11·69; three samples were optically inactive, whereas the fourth deviated the plane of polarisation slightly to the right, viz. + 0° 18′.

Niger seed is crushed in Hull and in Marseilles; the oil is used in soap-making as a substitute for linseed oil, and also for adulterating rape oil. The best qualities are employed as edible oil.[2] It is largely used in India by the poorer classes, especially in the Deccan, as a substitute for ghee butter.

[1] *Journ. Soc. Chem. Ind.* 1898, 991. [2] *Ibid.* 1905, 358.

Physical and Chemical Characteristics of Niger Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.		Viscosity.	
													Oleo-refractometer.			
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	° C.	Observer.	"Degrees."	Observer.	Seconds at 70° F.	Observer.
15·5 (water at 15·5 = 1)	0·9270	Allen Crossley and Le Sueur [1]	-9	Allen	189-191	Stoddard Crossley and Le Sueur [1]	132·9	Archbutt Wallenstein and Finck Crossley and Le Sueur	0·11-0·63	Crossley and Le Sueur [1]	82	Baynes Allen	+26 to +30 at 22° C.	Pearmain	263·1-292·6	Crossley and Le Sueur
99 (water at 15·5 = 1)	0·9248-0·9263				188·9-192·2		133·5				81					
	0·8738						126·6-133·8						Butyro-refractometer.			
													"Degrees." 63·0 at 40° C.	Crossley and Le Sueur		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Iodine Value of the Liquid Fatty Acids.	
Per cent.	Observer.	At 100° C. (water at 100 = 1).	Observer.	Per cent.	Observer.
94·11	Crossley and Le Sueur [1]	0·8886	Archbutt	147·5	Wallenstein and Finck.

[1] "East Indian Oils" (*Journ. Soc. Chem. Ind.* 1898, 991).

SUNFLOWER OIL

French—*Huile de tournesol.* German—*Sonnenblumenöl.*
Italian—*Olio di girasole.*

For tables of characteristics see p. 104.

This oil, obtained from the (*achenes*) seeds of *Helianthus annuus*, L., is a pale yellow oil of mild taste and pleasant smell. The sunflower plant is largely cultivated for oil-yielding purposes in Russia, Hungary, India, and China.[1] The Hungarian[2] kernels are richer in oil than the Russian. The Hungarian seeds consist of 45-52 per cent of kernels, and 48-55 per cent of husks. The kernels contain 36·6 to 53 per cent of oil. On a practical scale 28-30 per cent of oil are recovered. The Russian seeds yield only 23 per cent of oil. The cake contains from 8 to 10 per cent of oil, and is said to form, owing to its easy digestibility and fattening properties, a valuable cattle food, comparable in this respect with linseed oil.

Attempts made in the United States to grow the plant for commercial purposes (to prepare edible oil) have not proved satisfactory; the cultivation of the plant as an oil-producer has therefore been abandoned.

Experiments have also been made in India; but it was found that sunflower is too costly a crop to be grown there[3] as an oil-seed crop. Greater success appears to have attended the experiments made by the Cape Agricultural Department. In some cases a yield of 3250 lbs. of seed was obtained per acre; it is therefore proposed to undertake the cultivation of sunflower for its seed on a commercial scale.[4]

The cold-drawn oil is clear and limpid. On hot pressing the oil dissolves a considerable quantity of mucilaginous substances, similar in composition to the mucilage in linseed oil (see p. 48), which separate out on cooling. Hence the hot-pressed oil, if required as burning oil, etc., must be refined. The refining process consists in treating the oil with sulphuric acid, in the same manner as rape oil is refined.

Sunflower oil contains from 0·31 to 0·72 per cent of unsaponifiable matter; a specimen prepared by *Holde*[5] from sunflower seed by extraction with petroleum ether contained 5·6 per cent of free fatty acids (calculated to oleic acid). The liquid fatty acids consist chiefly of linolic acid, oleic acid being present in small quantities only.

[1] In the primitive mills of Manchuria (cp. "Soja Bean Oil") 26-27 per cent of oil are obtained by expression and 43-46 per cent of cakes, retaining 8-12 per cent of oil. This favourable technical result is due to the pounded seed being left in the wedge presses for more than twelve hours.

[2] R. Windisch, *Landw. Versuchs-Stat.* 1902, 305.

[3] D. Hooper, *The Agricultural Ledger*, 1907, No. 1.

[4] *Cape Agricultural Journ.* 1908 (25), 85, through *Bull. Imp. Inst.* 1908, 84.

[5] *Journ. Soc. Chem. Ind.* 1894, 892.

Physical and Chemical Characteristics of Sunflower Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	At 60° C.	Observer.
15	0·924-0·926	Allen	−16 to	Bornemann	193-194	Bornemann	129	Spüller	72-75	De Negri	1·4611	Thoerner
,,	0·926	De Negri and Fabris	−18·5 at −17	Holde	193-193·3	Spüller	122·5-133·3	Dieterich		and Fabris	Oleo-refractometer.	
,,	0·936	Dieterich	par-		188-189	De Negri and Fabris	119·7-120·2	De Negri and Fabris	67·5	Spüller	"Degrees."	Observer.
,,	0·9240	Holde	tially		193	Holde	135	Holde			+35 at 22° C.	Pearmain
90	0·919	,,	solid		193-194	Thoerner	129	Thoerner			Butyro-refractometer.	
											At 25° C.	Observer.
											72·2	Beckurts and Seiler

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
95	Spüller	17	Bach	23	Bach	201·5	Spüller	133·2-134	Spüller	1·4531	Thoerner
		18	Dieterich	23	Dieterich	201·6	Thoerner	124	De Negri and Fabris		
		18	De Negri and Fabris	17-22	Peters			124			
				22-24	De Negri and Fabris			133-134	Thoerner		
		17	Thoerner	23	Thoerner			Liquid Fatty Acids			
								154·3	Lewkowitsch		

This oil dries more slowly than those already described. The absorption of oxygen, according to *Hübl's* method, using copper powder as an oxygen carrier, takes place at the following rate :—

Absorption of Oxygen.	After 2 days.	After 7 days.	After 30 days.
	Per cent.	Per cent.	Per cent.
Sunflower oil	1·97	5·02	...
Sunflower oil fatty acids . . .	0·85	3·56	6·3

The sunflower is chiefly cultivated in Southern Russia,[1] where the "cold-drawn" oil serves for culinary purposes. Such oil is used in Russia in the manufacture of margarine (*Jolles*[2]). The hot-expressed oil is employed in soap-making, for the manufacture of Russian varnishes, and as a burning oil.

The extent of the sunflower seed and sunflower oil industry in Russia may be gathered from the fact that in the northern Caucasus[3] from 50,000 to 60,000 tons of sunflower cake are stated to have been produced during the year 1906. Most of the cake is sent to Denmark and Sweden, and the estimation in which the feeding properties of this cake are held may be gathered from the fact that the price the cake realised was between that of linseed cake and cotton seed cake. The seed stalks are burnt, and the carbonate of potash, which the ashes yield in considerable quantity, is exported. It is stated that in the year 1905, 2000 tons of crude carbonate of potash from this source were exported.

YELLOW ACACIA OIL[4]

French—*Huile d'acacia jaune.* German—*Gelb-Akazienöl.*
Italian—*Olio di acacia gialla.*

This oil is obtained from the seeds of the yellow acacia, *Caragaena arborescens*, Lam., largely cultivated in South Russia. The seeds yield 12·4 per cent of oil on extraction with petroleum ether. The unsaponifiable matter in the oil amounts to only 0·14 per cent.

Physical and Chemical Characteristics of Yellow Acacia Oil.

Saponification Value.	Iodine Value.	Reichert-Meissl Value.
190·6	128·9	2·7

[1] *Journ. Soc. Chem. Ind.* 1892, 470. [2] *Ibid.* 1893, 935. [3] Kuban district.
[4] Valentin Jones, *Mittheil. d. k. k. technolog. Gewerbe-Museums*, 1903, 223.

Physical and Chemical Characteristics of the Insoluble Fatty Acids.

Insoluble Acids + Unsaponifiable.	Neutralisation Number.	Mean Molecular Weight.	Iodine Value.
93·94	199·0	280·9	131·7

By means of the lead-salt-ether method 8·74 per cent of solid fatty acids were obtained. Amongst these were identified palmitic, stearic, and erucic acids. The liquid fatty acids consisted of oleic and linolic acids. The less pronounced drying power of this oil, as compared with white acacia oil, is explained by the absence of linolenic acid.

PARA RUBBER TREE SEED OIL—RUBBER SEED OIL

French—*Huile de siphonia elastica*, *Huile d'Hevea*. German—*Parakautschukbaumsamenöl*, *Paragummibaumöl*. Italian—*Olio (d' albero) di cacciù*.

For tables of characteristics see p. 107.

This oil is obtained from the kernels of the para rubber tree (*Hevea brasiliensis*, Müller Arg.). The nuts contain about 50 per cent of kernels. They also contain a powerfully acting lipolytic enzyme (*Imperial Institute*) and a cyanogenetic glucoside resembling phaseolunatin.[1] Several samples of seeds examined in the Imperial Institute were found to yield about 0·048 per cent of prussic acid[2] (cp. "Linseed Oil," p. 48), so that if the seeds were expressed the resulting cake would yield about 0·09 per cent of prussic acid.

The kernels yielded to petroleum ether 42-49 per cent of oil.[3] *Schroeder*[4] obtained, by extracting with petroleum ether, 27·5 per cent only of oil. On extracting the kernels on a larger scale with ether 24·32 per cent of oil were recovered. But whereas the oil extracted with petroleum ether was pale yellow, the ether-extracted oil represented a deep green semi-solid oil from which, at 15° C., solid glycerides separated. On warming to 26° C. the oil became completely fluid, and on cooling solid glycerides again separated at 21° C. A notable difference between the oil extracted with petroleum ether and the oil extracted with common ether is shown by the differing iodine values (compare table). The acid value of the ether-soluble sample was 57·4, its acetyl value 27·9, and the proportion of unsaponifiable matter 0·705 per cent.

Amongst the fatty acids stearic and palmitic acids were identified.

The oil is of a light yellow colour, and has an odour resembling that of linseed oil. When exposed to the atmosphere it dries to

[1] Dunstan, *Proc. Chem. Soc.* 1907, 168.
[2] Henry and Auld, *Journ. Soc. Chem. Ind.* 1908, 428.
[3] *Bull. Imp. Inst.* 1903, 156. [4] *Arch. f. Pharm.* 1905, **243**, 637.

a clear transparent film. A specimen examined in the Imperial Institute contained 5·4 per cent of free fatty acids.

Physical and Chemical Characteristics of Para Rubber Tree Seed Oil

Specific Gravity.		Saponification Value.	Iodine Value.	Observer.
°C.				
15	0·9302	206·1 [1]	128·3 [1] 127·7 [1]	Imperial Institute
20	0·9232	198·1	117·6 [2]	Schroeder

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Mean Molecular Weight.	Iodine Value.	Observer.
95·06	293·3	127·3	Schroeder

The manufacture of a drying oil from the seeds is not likely to be undertaken in the near future, the seeds being all required for planting purposes in the now rapidly developing Para rubber industry in East India and East Africa. According to a reliable estimate,[3] there are now in Ceylon 45,000 acres under crop, or, at 175 plants to the acre, 7,875,000 plants of various ages.

SERVICE BERRY OIL—MOUNTAIN ASH BERRY OIL

French—*Huile de sorbier sauvage.* German—*Vogelbeerenöl.*
Italian—*Olio di sorba salvatica.*

The seeds of *Sorbus aucuparia*, L. (Service Berry ?)[4] contain 21·9 per cent of a fatty oil. The oil has a sweetish taste, is slightly yellowish, and dries on exposure to the air.

10 grms. of the seeds freed from oil gave 7·29 mgrms. hydrocyanic acid. The oil had the following characteristics :—

Specific gravity at 15° C.	0·9137
Refractive index at 15° C.	1·4753
Saponification value	208·0
Iodine value	128·5
Iodine value of the insoluble fatty acids	127·5
Neutralisation value of the insoluble fatty acids	230·2

[1] Extracted with petroleum ether. [2] Extracted with ether.

[3] *Ceylon Handbook and Directory and Compendium of Useful Information for* 1905-1906, compiled and edited by J. Ferguson. Colombo : A. and J. Ferguson ; reviewed in *Bull. Imp. Inst.* 1906, vol. iii. No. 4, p. 384.

[4] L. van Itallie and C. H. Nieuwland *Arch. Pharm.* 1906, **244**, 164.

CELOSIA OIL [1]

French—*Huile de Celosia.* German—*Celosiaöl.*
Italian—*Olio di celosia.*

This oil is obtained from the seeds of *Celosia cristata*, L., a plant indigenous to the East Indies and China; it is a greenish-brown drying oil.

Physical and Chemical Characteristics of Celosia Oil

Solidifying Point.	Saponification Value.	Iodine Value.
− 10° C.	190·5	126·3

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.
21°-19° C.	27°-29° C.

ARGEMONE OIL [2]

French—*Huile de pavot épineux.* German—*Argemoneöl.*
Italian—*Olio di argemona.*

Physical and Chemical Characteristics of Argemone Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. At 40° C.	Viscosity in Redwood's Viscosimeter.	Insoluble Acids + Unsaponifiable.
At 15·5° (water 15·5 = 1).	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refractometer. "Degrees."	Number of Seconds at 70° F.	Per cent.
0·9247-0·9259	187·8-190·3	119·91-122·5	0·00	62·5	268·9-272	95·07

Argemone oil is expressed from the seeds of *Argemone mexicana*, L., the Mexican or prickly poppy. The fresh oil is of orange colour, and has a slight, but distinctive smell (see Appendix).

Volatile acids — acetic, butyric, and valeric—which have been stated to occur in Argemone oil could not be detected in the two genuine specimens examined by *Crossley* and *Le Sueur*. These oils

[1] De Negri and Fabris, *Chem. Zeit.* 1896, Rep. 161.
[2] Crossley and Le Sueur, *Journ. Soc. Chem. Ind.* 1898, 991.

had the acid values 6·0 and 83·9 respectively. Hence the second specimen was completely soluble in 9 to 10 volumes of absolute alcohol at the ordinary temperature.

Argemone oil is used as an edible oil in the East Indies, where it can be obtained in practically unlimited quantities. In the West Indies and in Mexico the oil is used as a lubricant and illuminant.

The seeds of *Argemone albiflora*, *A. speciosa*, *A. grandiflora*, *A. hispida*, and *A. Hunnemannii* from Curaçoa, Cape Verde, and St. Eustatius yield about 37 per cent of a fatty oil. The oil extracted from *A. speciosa* by means of carbon tetrachloride had the specific gravity 0·9435 at 15° C., the saponification value 200·2, the iodine value 113·3,[1] and gave a deep red coloration with nitric acid.

FIR SEED OIL

French—*Huile de pignon.* German—*Fichtensamenöl.*
Italian—*Olio di pinoli.*

For tables of characteristics see p. 110.

Fir seed oil is obtained from the seeds of several kinds of pine-trees—*Pinus sylvestris*, L. (Scotch fir seed), *Pinus picea*, L., and *Pinus abies*, L.[2] The seeds contain from 32 per cent to 33 per cent of oil.

This oil is of pale yellow colour (Scotch fir seed oil is brownish yellow), and has a sweet taste.

Fir seed oils are stated to dry readily, and may therefore be useful in the preparation of varnishes.

The following are the characteristics of the oils obtained from the various kinds of seeds :—

[1] W. H. Bloemendal, *Pharm. Weekblad*, 43 (1906), 342.

[2] The fatty oil from *Pinus monophylla* (?) is described as *Pine nut oil* by Blasdale (*Journ. Soc. Chem. Ind.* 1896, 205). It is a brown drying oil with an unpleasant odour and taste. The following characteristics are given :—

Physical and Chemical Characteristics of Pine Nut Oil

Spec. Grav. at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.	Refractive Index.
0·933	192·8	101·3	71° C.	1·4769

Melting point of the mixed fatty acids, 19° C.

Physical and Chemical Characteristics of Fir Seed Oil

Source.	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
Pinus sylvestris .	15	0·9312	De Fontenelle	– 27 to – 30	De Fontenelle						
Pinus abies [1] . .	,,	0·9285	,,								
Pinus picea . .	,,	0·9215	De Negri and Fabris	– 18 to – 20	De Negri and Fabris	191·3	De Negri and Fabris	118·9-120	De Negri and Fabris	98-99	De Negri and Fabris

[1] The *Huile de sapin* is obtained from this tree.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Source.	Solidifying Point.		Melting Point.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Pinus picea, expressed . . .	10-15	De Negri and Fabris	16-19	De Negri and Fabris	121·5	De Negri and Fabris
,, ,, extracted . . .	12-16	,,	17-19	,,		

MADIA OIL

French—*Huile de Madia.* German—*Madiaöl.*
Italian—*Olio di Madia.*

For tables of characteristics see p. 112.

Madia oil is obtained from the seeds of the Chilian *Madia sativa*, Mol. This plant was cultivated successfully in South Germany on an experimental scale; these experiments have, however, been discontinued. The seeds contain 32-33 per cent of oil. This oil is dark yellow, and has a characteristic, not unpleasant odour.

Madia oil occupies an intermediate place between drying and semi-drying oils. Treated with nitrous acid (elaïdin test) it remains liquid; for this reason, as also on account of its high iodine value, I have placed it amongst the drying oils. It absorbs, indeed, considerable quantities of oxygen, thereby becoming viscid.

The oil is chiefly used for burning; it is also used for soap-making. The cold-pressed oil is employed for edible purposes.

Physical and Chemical Characteristics of Madia Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·926-0·928	Hartwich	−10 to −17 (by hot pressure)	Winkler	192·8	De Negri and Fabris	117·5-119·5	De Negri and Fabris	95-99	De Negri and Fabris
0·9285	De Negri and Fabris	−22·5 (cold-drawn)	Riegler						
0·9286	Winkler	−12 to −15	De Negri and Fabris						

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
20-22	De Negri and Fabris	23-26	De Negri and Fabris	120·7	De Negri and Fabris

Lesser Known Drying Oils

STRAWBERRY SEED OIL

French—*Huile de fraisier.* German—*Erdbeerenöl.*
Italian—*Olio di fragola.*

Strawberry seeds contain 19·02 per cent of a fatty oil (*Anarin*[1]), stated to dry as quickly as linseed oil. The iodine value of the insoluble fatty acids is 191-193. The acids consist of 81 per cent linolic, and 10·5 linolenic and oleic acids. (See Appendix.)

Physical and Chemical Characteristics of Strawberry Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index at 25°.
0·9345	193·7	180·3	2·1	1·4790

RASPBERRY SEED OIL

French—*Huile de framboisier.* German—*Himbeerkernöl.*
Italian—*Olio di lampone.*

The seeds of the raspberry contain 14·6 per cent of a strongly drying oil, which in *Livache's* test[2] absorbs 8·4 per cent of oxygen after two days. The liquid fatty acids consist chiefly of linolic and linolenic acids, linolic preponderating, and of small quantities of oleic and isolinolenic acids. The acid value of the specimen of oil was 1·0. The unsaponifiable matter yielded 0·73 per cent (calculated to the oil) of phytosterol, of the melting point 134·5° C.

Physical and Chemical Characteristics of Raspberry Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9317	192·3	174·8	0·0

[1] Prot. *Russ. Phys. Chem. Soc.* 1903, 213; *Chem. Centrlb.* 1904, ii. 459.
[2] Kržižan, *Zeit. f. öffentl. Chemie,* 13 (1907), 263; cp. J. Kochs, *Jahresb. d. Versuchss. d. K. Gärtnerlehranst.*, Dahlem.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity at 15° C.	Neutralisation Value.	Iodine Value.
0·9114	197·2	181·3
	Liquid Fatty Acids.	
	200·8	185·9

HAWTHORN SEED OIL. See Appendix.

CURRANT SEED OIL. See Appendix.

BLACKBERRY SEED OIL [1]

French—*Huile de ronce.* German—*Brombeerkernöl.*
Italian—*Olio di more.*

For tables of characteristics see p. 115.

This oil occurs to an extent of 12·6 per cent in the seeds of the blackberry. The oil obtained by extraction with petroleum ether is dark green to yellowish, and shows in reflected light a red fluorescence. The green colour is due to chlorophyll. This green colour seems to be difficult to remove, for the liquid fatty acids prepared by the lead-salt-ether method still exhibit an emerald-green colour with red fluorescence. The oil had an acid value of 2·03. The fatty acids were resolved by means of the lead-salt-ether method into 4·7 per cent of solid, and 91 per cent of liquid acids.

The solid fatty acids melt, after crystallisation from alcohol, at 61·5° C., and probably consist of palmitic acid. The liquid fatty acids were exhaustively examined by *Hazura's* method, and from the amount of the oxidation products obtained, the following approximate composition of the liquid fatty acids was derived :—

	Per cent.
Oleic acid	17
Linolic acid	80
Linolenic acid	about 1·5
Isolinolenic acid	,, 1·5

The unsaponifiable matter in the oil amounted to 0·83 per cent; 0·6 per cent were obtained as crystallised (phytosterol) sitosterol, of the melting point 133° C. The oil has distinct drying powers, for in the *Livache* test it showed after three days an increase in weight of 6·87 per cent. The oil dries somewhat less rapidly than raspberry seed oil.

[1] Kržižan, *Chem. Revue*, 1908, 7.

Physical and Chemical Characteristics of Blackberry Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9256	189·5	147·8	0·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity at 15° C.	Insoluble Fatty Acids + Unsaponifiable. Per cent.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.
0·9070	96·3	280·9	155·1	13·9
		Liquid Fatty Acids.		
		281·3	163·2	

INDIAN LAUREL OIL [1]

French—*Huile de laurier indien.* German—*Indisches Lorbeeröl.*
Italian—*Olio di lauro indico.*

The fruits from *Laurus indica* yield a brown viscous oil. The specimen examined contained 33 per cent of free fatty acids.

Physical and Chemical Characteristics of Indian Laurel Oil

Specific Gravity at 15° C.	Solidifying Point.	Saponification Value.	Iodine Value.
0·926	Thickens at −15° C., but does not solidify.	170	118·6

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.
19°-18° C.	24°-26° C.

[1] De Negri and Fabris, *Chem. Zeit.* 1896, Rep. 161.

TOBACCO SEED OIL

French—*Huile de tabac.* German—*Tabaksamenöl.*
Italian—*Olio di tabacco.*

The seeds of *Nicotiana Tabacum*, L., yield, on pressing, 9-10 per cent, and, by extraction, 30-32 per cent of a pale greenish-yellow oil, having a pleasant odour differing from that of tobacco. The specimens examined by *Ampola* and *Scurti*[1] contained 3·49 per cent of free fatty acids.

In the elaïdin test the oil remained liquid, and a whitish precipitate was produced. The oil is stated to have strong drying powers. In *Livache's* test it absorbs after two days 5·01 per cent of oxygen, and after three days 5·6 ; after four days 5·84, and after fourteen days 6·84 per cent. The fatty acids of the oil are stated to consist of 25 per cent oleic acid, 15 per cent linolic acid, and 32 per cent palmitic acid, together with small quantities of stearic acid.

Physical and Chemical Characteristics of Tobacco Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.
0·9232 (Schübler)	190	118·6	100° C.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Mean Molecular Weight.
Per cent. 94·73	203

WELD SEED OIL

French—*Huile de gaude.* German—*Resedasamenöl, Wausamenöl.*
Italian—*Olio di guaderella.*

This oil is obtained from the seeds of the dyer's weld, *Reseda luteola*, D.C. Owing to the presence of chlorophyll, the oil has a dark greenish tint. Its specific gravity is 0·9358 (*Schübler*); its solidifying point −20° C. It has a bitter taste and nauseous odour. The oil dries easily on exposure to air. It is used as a burning oil and for making varnishes.

[1] *Gaz. Chim. Ital.* 1904, **34**, 315.

ISANO (UNGUEKO) OIL [1]

Isano (I'Sano) oil is obtained from the seeds of the I'Sano [2] or Ungueko,[3] a large tree of the family *Oleaceæ*, growing in the French Congo. The ground and dried seeds yield 60 per cent of oil.

The specific gravity of the oil is 0·973 at 23° C. It is liquid even at − 15° C., is reddish in colour, has an insipid flavour and fishy smell. The oil is viscous and possesses strong drying powers. Tested by *Maumené's* test it gives a thermal reaction of 115° C. The bromine value is stated to be double that of oleic acid. It is further stated that the oil contains 86 per cent of liquid fatty acids (the lead salts being entirely soluble in ether), consisting of 15 per cent oleic acid, 75 per cent linolic acid, and 10 per cent of isanic acid (Vol. I. Chap. III.). On saponification from 12 to 13 per cent of glycerol are said to be obtained.

MOHAMBA OIL [1]

The seeds yielding mohamba oil are very similar to those of the Isano tree, but after drying they give only 12 per cent of oil.

The oil has the specific gravity of 0·915 at 23° C.; it remains liquid at − 15° C., is of yellow colour, fairly fluid, inodorous, and of insipid taste. In *Maumené's* test the oil gave a rise of 55° C.

On saponification about 9 per cent of glycerol and 90 per cent of brown, unsaturated (liquid) fatty acids are obtained. From the lead salts of the acids, which are entirely soluble in ether, there was obtained, on separating the free acids, a white fatty acid, soluble in alcohol and ether, and crystallising from the latter in laminæ, melting at 34°-35° C. This acid absorbs about as much bromine as oleic acid does, and would therefore belong to the oleic series, but does not seem to be identical with any known acid. The liquid acids appear to consist of oleic acid, as they absorb an amount of bromine corresponding to oleic acid and give the elaïdin reaction.

(2) Semi-Drying Oils

The oils comprised in this class form an intermediate link between the drying and the non-drying oils; this is readily shown by their iodine values, which lie between those of the drying oils and the non-drying oils.

Chemically they differ from the drying oils by the absence of linolenic acids, whilst they are differentiated from the non-drying oils by the linolic acid they contain. The proportion of linolic acid

[1] Hébert, *Journ. Soc. Chem. Ind.* 1896, 660. Cp. Heckel, *Les graines grasses nouvelles ou peu connues des colonies françaises.* Paris, 1902.

[2] Local name in Loango (from *Onguekoa Gore*, Engl.; *Ongokea Klaineana*, Pierre).

[3] Local name.

decreases as the iodine values decrease. The members of this class appear to range themselves naturally into two groups :—

(α) Cotton Seed Oil Group
(β) Rape Oil Group.

(α) The Cotton Seed Oil Group

The members of this group still possess distinct drying properties, although they are less pronounced than in the case of the true drying oils.

The drying power becomes more apparent on allowing the oils to dry at a somewhat elevated temperature. At the ordinary temperature maize oil and cotton oil form a viscous mass after exposure to the atmosphere for several weeks in thin layers. This group takes its name from its most prominent member, which may be considered as the type of a semi-drying oil ; it contains a notable amount of linolic acid.

CAMELINE OIL (GERMAN SESAMÉ OIL)

French—*Huile de cameline.* German—*Deutsches Sesamöl, Leindotteröl, Rüllöl.* Italian—*Olio di cameline.*

For tables of characteristics see p. 119.

Cameline oil is obtained from the seeds of *Myagrum sativum*, Crz. (or *Camelina sativa* (L.), Fr.), belonging to the *Cruciferæ*.

Several centuries ago the seed was grown all over Germany as a crop. At present it is harvested in some parts of South Germany, Belgium, Holland, Hungaria, the Balkan States, and South Russia. Press cakes are shipped to this country (Liverpool) from Odessa, and are used in the manufacture of compound cakes. The seeds contain 31-34 per cent of an oil of a golden-yellow colour and a pungent taste and smell. On exposure to the air the oil dries slowly. Boiled with litharge or manganese borate it yields a slowly drying varnish.

The low saponification value points to the presence of glycerides of erucic acid. The oil prepared by expression is free from sulphur, like all the oils drawn in the cold from seeds of the *Cruciferæ* (cp. "Rape Oil," p. 212).

On account of its low price the oil is not likely to be adulterated. It is used, however, for the adulteration of rape oil, in which it may be detected by a high iodine value. Cameline oil is naturally present in linseed oil expressed from East Indian seed (cp. p. 43).

The cold-drawn oil is occasionally employed for edible purposes. Its chief use, however, is for soap-making. It suitably replaces linseed oil for making soft soap during the winter. In summer, however, cameline oil cannot be used alone, its potash soap being liquid at a temperature below 20° C.

Physical and Chemical Characteristics of Cameline Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees" at 22° C.	Observer.
0·9260	Christiani	−18	Chateau	188	De Negri and Fabris	135·3	De Negri and Fabris	117	De Negri and Fabris	+32	Jean
0·9259	Massie					142·4	Tortelli and Ruggeri	82	Jean		
0·9252	Schübler										
0·9260	De Negri and Fabris										
0·9200	Levallois										
0·9240	Jean										

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
14-13	De Negri and Fabris	18-20	De Negri and Fabris	136·8	De Negri and Fabris
				Iodine Value of Liquid Fatty Acids.	
				165·4	Tortelli and Ruggeri

CELANDINE OIL, SWALLOW-WORT OIL

French—*Huile de chélidoine.* German—*Schöllkrautöl.*
Italian—*Olio di celidonia.*

This oil has been obtained from the seeds of *Chelidonium majus*, L., which contain 46·6 per cent of oil. The specimen examined by *Fokin* [1] had undergone hydrolysis to a considerable extent, as evidenced by its high proportion of free fatty acids, viz., 50·4 per cent.

Fokin states that the oil contains no linolic acid.

Physical and Chemical Characteristics of Celandine Oil

Specific Gravity.		Saponification Value.
At ° C.		Mgrms. KOH.
19 (water 19° = 1)	0·917	198·2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.		Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.
At ° C.		° C.	° C.	Mgrms. KOH.	Per cent.
19 (water 19° = 1)	0·902	6-4	7-16	201·1	127·3

DAPHNE OIL [2]

French—*Huile de Daphne.* German—*Daphneöl.*
Italian—*Olio di daphne.*

This oil is obtained from the seeds of *Daphne Cnidium*, L. (*semen coccognidii*), and other Daphne species such as *D. Mezereum.* The seeds contain from 36-37 per cent of oil; the oil has a greenish-yellow colour, and dries on exposure to the atmosphere.

The solid fatty acids of the oil consist of palmitic and stearic acids; the statement that the liquid fatty acids contain besides oleic

[1] *Chem. Revue*, 1906, 130. [2] Peters, *Arch. Pharm.* 1902, 240.

and linolic acids also linolenic and isolinolenic acids requires confirmation.

Physical and Chemical Characteristics of Daphne Oil

Specific Gravity at 15° C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9237	196·5	126·1

CLOVER OIL (RED CLOVER OIL; WHITE CLOVER OIL)

French—*Huile de trèfle.* German—*Kleesamenöl.*
Italian—*Olio di trifoglio.*

This oil is obtained from the seeds of the clover, *Trifolium.* Two species of clover seed, viz. *Trifolium pratense perenne*, L., red clover, and *Trifolium repens*, L., white clover, were examined by *Valentin Jones.*[1] The seeds of the red clover yielded 11·1 per cent, and the seeds of the white clover 11·8 per cent of oil on extraction with petroleum ether.

Physical and Chemical Characteristics of Clover Oil

Clover Oil.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
Red . . .	189·9	124·3	3·3
White . .	189·5	119·7	3·5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Clover Oil.	Insoluble Acids +Unsaponifiable.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
Red . .	93·62	198·1	283·2	126·2
White . .	93·24	197·6	283·8	122·2

The solid fatty acids of red clover oil consist of palmitic and stearic acids. The liquid fatty acids contain oleic and linolic acids, the former predominating.

White clover oil resembles very closely in its chemical composition the red clover oil. The lower iodine value points to a smaller proportion of liquid fatty acids in white clover oil.

[1] *Mitth. d. K. K. technolog. Gewerbe Museums*, 1903, 223.

SOJA BEAN OIL (SOY-BEAN OIL, BEAN OIL, CHINESE BEAN OIL)

French—*Huile de soja*, *Huile de soya*. German—*Saubohnenfett*, *Sojabohnenöl*, *Chinesisches Bohnenöl*. Italian—*Olio di soia*.

For tables of characteristics see p. 123.

This oil is obtained from the seeds of *Dolichos soja*, L., *Soja hispida*, Sieb. et Zuc., *Soja japonica*, *Glycine hispida*, Maxim, a plant indigenous to China, Manchuria, Korea, Japan, Formosa, and Indo-China,[1] where the oil and the expressed cake are largely used for edible purposes. The seeds contain 18 per cent of oil and about 30-40 per cent of proteïns.[2]

The industry of the soja bean forms one of the most important manufactures of Manchuria [3] and of Japan.

In China three varieties of soja (*téon*) are known, namely, yellow (*houang*), green (*tsin*), and black (*hei*). In Manchuria the beans are soaked in water over night, then crushed and boiled with a little water, so as to burst the oil cells. The oil is then expressed in the most primitive fashion; but owing to the long time the cakes are allowed to remain in the presses the yield of oil amounts to 13 per cent, whereas experiments made with modern machinery are said to have yielded no more than 10 per cent. The expressed meal is made into bean-cakes (Chinese, *Téou-fou-tcha*), which constitute one of the staple foods of the country, and form an important article of export. Thus in 1903 there were shipped from Newchwang alone 196,680 tons of beans, 6000 tons of soja bean oil, and 273,000 tons of bean cake.[4]

The plant is also extensively cultivated in Japan.[5] The extent of the soja bean industry in Japan may be gathered from the fact that there exist in that country no less than 11,000 installations, in which about two and a half millions hectolitres of beans are expressed and treated per annum, by a kind of fermentation (with the aid of *Aspergillus oryzæ*), for the preparation of soja (Japanese, *Shojou* or *Misou*), a liquid condiment extensively used by the population.[6] The demand for soja is so great that the home production, estimated at five to seven millions hectolitres of beans per annum, does not suffice, and therefore beans are imported from Manchuria and Korea. In the year 1904 there were imported 160,000 tons of beans (to which must be added bean oil and bean cake). Efforts have been made to ship soja beans to Europe, but on account of the deterioration which they undergo on the long voyage, as also on account of the difficulty of disposing of the cakes, attempts in this direction have been abandoned.

[1] *Bulletin Économique de l'Indo-Chine*. December 1905. *Les cultures vivrières au Tonkin*. Hanoï, 1905.

[2] O. Nagel, *Journ. Soc. Chem. Ind.* 1903, 1337. For soja bean preparations see K. Saito, *Zentrlblatt f. Bakterien und Parasitenkunde*, ii. 17 (1906), 20, 101, 152.

[3] A. Hosie, *Manchuria*, Methuen and Co., London, 1901. Cp. also *Journ. Soc. Chem. Ind.* 1893, 769; 1901, 642. [4] These statistical data are not reliable.

[5] Pozzi-Escot, *Revue gén. de chim. pur. et appl.* 1902, 64.

[6] Cp. Suzuki, Aso, and Mitarai, *Bull. Coll. Agric. Tokyo Imp. Univ.* 1907, **7**, 477. An apparatus for preparing soy sauce has been patented by Suzuki, French patent 377,294.

Physical and Chemical Characteristics of Soja Bean Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9270	Morawski and Stingl	+15 to +8	De Negri and Fabris	192·9	Morawski and Stingl	122·2	Morawski and Stingl	61	Morawski and Stingl
0·9242	De Negri and Fabris			192 5	De Negri and Fabris	121·3	De Negri and Fabris	59	De Negri and Fabris
0·924	Shukoff[1]			190·6	Shukoff	124	Shukoff		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
95·5	Morawski and Stingl	25	Morawski and Stingl	28	Morawski and Stingl	115·2	Morawski and Stingl
		25-23	De Negri and Fabris	27-29	De Negri and Fabris	122	De Negri and Fabris
		24·1	Shukoff				
						Liquid Fatty Acids.	
						131	Lane

[1] From seed grown in an experimental station in South Russia.

A sample of the oil extracted with ether by *Morawski* and *Stingl* gave 2·28 per cent of free acids calculated to oleic acid, and 0·22 per cent of unsaponifiable matter. According to *Klobb* and *Bloch*,[1] the unsaponifiable matter consists of *sojasterol*.

The proportion of solid fatty acids in the oil is approximately 11·5 per cent of the total mixed fatty acids; *Lane* found 80·26 per cent of liquid fatty acids. The bulk of the solid fatty acids is stated to consist of palmitic acid; the liquid fatty acids consist of oleic and linolic acids.

On exposure to air the oil dries slowly with the formation of a thin skin.

The oil is chiefly used in the Far East as food and as an illuminant.

PUMPKIN SEED OIL

French—*Huile de courge, huile de potiron.* German—*Kürbissamenöl, Kürbiskernöl.* Italian—*Olio di zucca.*

For tables of characteristics see p. 125.

Pumpkin seed oil is obtained from the seeds of *Cucurbita pepo*, L., by cold expression. In South Russia the oil is prepared on a commercial scale by roasting the seeds and subsequently expressing the oil in the hot.[2]

The seeds consist of 23·5 per cent husks and 76·5 per cent kernels ("meats"). The whole seeds contain from 35 to 37·5 per cent of oil; the kernels yield from 47 to 48 per cent of oil.

The oil obtained by cold expression has a greenish colour with a faint red fluorescence, whilst that prepared commercially, as described above, is stated to be viscous and of a brownish-green colour by transmitted light, and of a deep red colour in reflected light. It should be noted that the seeds pass through various stages of drying or roasting, which no doubt exercise a considerable influence on the colour of the oil.

The characteristics obtained by *Poda* for oils prepared by himself by both methods agree closely with those yielded by commercial oils.

The oil has considerable drying properties.

Strauss[3] attempted to bleach the oil (obtained by expressing the crushed seeds after heating them to 80°-90° C.) with concentrated sulphuric acid, chlorine, ozone, and sulphurous acid, but the results were not satisfactory. Other experiments, having for their object the refining of the oil with caustic soda, yielded a pale oil, but the losses due to saponification were very considerable.

[1] *Bull. Soc. Chim.* (4), i. 422. [2] Poda, *Journ. Soc. Chem. Ind.* 1898, 1054.
[3] *Chem. Zeit.* 1903, 527.

Physical and Chemical Characteristics of Pumpkin Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Butyro-refractometer at 25° C. "Degrees."	Observer.
15	0·923-0·925	Poda [2]	−16	Schattenfroh	188·7	Schattenfroh	121	Hübl	70·2-72·5 [1]	Poda
15·5	0·9197	Graham [5]			188·4-190·2	Poda [2]	121·5	Henriques	70-72·5 [2]	,,
20	0·923	Schattenfroh					113·4	Schattenfroh		
							122·8-130·7	Poda [2]		
							120·5	Strauss		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Mean Molecular Weight.	
Per cent.	Observer.	°C.	Observer.		Observer.
96·2	Schattenfroh	26·5-28·5 [3]	Poda	284·7	Schattenfroh
		28·4-29·8 [4]	,,		

[1] Mean values of cold-pressed and hot-pressed oil (*Journ. Soc. Chem. Ind.* 1898, 1054). [2] Ten commercial oils.
[3] Point of incipient fusion. [4] Point of complete fusion. [5] *Amer. Journ. Pharm.* 1901, 352.

The cold-drawn oil is used for edible purposes in Austria, Hungary, and Russia; it is stated that the oil from the large cucumber grown on the Slave Coast surpasses olive oil in flavour. The edible oil is adulterated with linseed, cotton seed, sesamé, and rape oils. Linseed oil would be detected by its high iodine value and the bromide test; cotton seed oil by the *Halphen* colour reaction (see p. 162); sesamé oil by the *Baudouin* colour reaction (see p. 176); rape oil by a low iodine value, in conjunction with a lower saponification value.

The lower qualities of pumpkin seed oil serve as a burning oil.

WATER-MELON OIL

French—*Huile de pastèque* (*huile de citrouille*[1]), *huile de gros béraff* (*béreff*).
German—*Wassermelonenöl.* Italian—*Olio di citriuolo.*

This oil is obtained from the kernels of *Cucumis citrullus, L.* (*Cucurbita citrullus*). The seeds yield 62 per cent kernels, which in their turn give 65·8 per cent of oil; hence the seeds contain 40·8 per cent of oil.

A specimen of oil examined by *Wijs*[2] contained 1·20 per cent free fatty acids; it gave the characteristics recorded in the table.

The oil gives neither the *Halphen* nor the *Baudouin* reactions.

Physical and Chemical Characteristics of Water-melon Oil

Specific Gravity.	Saponification Value.	Iodine Value.
At 20° C. (Water at 4° = 1).	Mgrms. KOH.	Per cent.
0·9160	189·7	118

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Number.	Saponification Value.	Mean Molecular Weight.	Iodine Value.
°C.	°C.	Mgrms. KOH.	Mgrms. KOH.		Per cent.
Titer Test.					
32	34	197·1	197·1	284·1	122·7

[1] It should be noted that the name "huile de citrouille" would also apply to "pumpkin seed oil."

[2] *Zeits. f. Unters. d. Nahrungs- und Genussm.* 1903, 492.

MELON SEED OIL [1]

French—*Huile de melon, huile de petit béraff (béreff).*
German—*Melonenöl.* Italian—*Oleo di mellone.*

Physical and Chemical Characteristics of Melon Seed Oil

Solidifying Point. °C.	Melting Point. °C.	Saponification Value.	Iodine Value.
5·5	5	193·3	101·5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. °C.	Melting Point. °C.
36	39

Melon oil is obtained from the seeds of *Cucumis melo*, L.; the seeds form an article of commerce on the Slave Coast and Gold Coast of West Africa. The seeds examined by *Fendler* contained 43·8 per cent of oil.

The specimen of oil examined had the acid value of 4·81.

Lidoff describes a melon seed oil obtained in the south of Russia by expressing the seeds. The oil is used for edible purposes, but is not an article of commerce. The numbers obtained by *Lidoff* deviate so much from those given by both water-melon oil and *melon seed oil* that they have not been tabulated. His results are as follows:—

Yield of oil by extraction	29·4 per cent
Specific gravity of the oil at 15·25° C.	0·9276
Saponification value	190·5
Iodine value	133·3
Percentage of insoluble acids + unsaponifiable matter	95·3 per cent
Iodine value of the fatty acids	128
Viscosity at 70° C. in Engler's apparatus (water = 1)	8·9
Acid value of the sample	1·37

Lidoff also found a high acetyl value. His conclusion, that the proportion of hydroxy acids in the oil is large, must be accepted with reserve (cp. Vol. I. Chap. V.).

[1] *Zeits. f. Unters. d. Nahrungs- und Genussm.* 1903, 1025.

MAIZE OIL, CORN OIL

French—*Huile de mais.* German—*Maisöl.* Italian—*Olio de mais, Olio di granturco.*

For tables of characteristics see pp. 131-133.

This oil is obtained from the germs of the maize plant, *Zea Mays*, L. The germs are recovered, in the process of manufacturing starch, by sifting and winnowing them from the starch granules in which they are imbedded. The oil is therefore a by-product of starch and glucose works using maize (corn) as their raw material.

Formerly maize oil was obtained as a by-product in the alcohol distilleries. When the malted and crushed grain was allowed to ferment, the oil was laid bare and rose to the top in the fermentation vats. Before distilling off the alcohol the oil was ladled off and purified in a crude fashion by washing, filtering, and "settling." Since, however, the presence of the germ imparts an unpleasant flavour to the spirit obtained by fermentation, and the oil so recovered was very impure, and had a different character from the oil expressed from the germs, the older process of fermenting the crushed grain has been abandoned. Nowadays the corn is first malted, then crushed, beaten up with water to a fine pulp, and the germ separated from the starch by sieving. At present, maize oil is manufactured on a very large scale from the isolated germs by expression in hydraulic presses. In a dry condition the germs contain 53 per cent of oil, and yield in practice about 40 per cent. The whole grain contains 4-10 per cent of oil.

At the St. Louis Exhibition, 1904, the author saw a collection (arranged by the State of Illinois), demonstrating experiments made at the Agricultural Experiment Station of Illinois at Champaign, where for a number of years it was attempted to produce two kinds of grain, one containing a large percentage of oil, and a second containing small percentages of oil. The result of these experiments, which had been protracted during seven generations of seeds, is shown in the following table :—

Year.	Grains containing High Percentage of Oil.	Grains containing Low Percentage of Oil.
1896	4·70	4·70
1897	4·73	4·06
1898	5·15	3·99
1899	5·64	3·82
1900	6·10	3·95
1901	6·09	3·43
1902	6·41	3·01
1903	6·53	2·97

The cake, which results as a by-product in the expression of the germs, is sold as cattle food of somewhat inferior value.

Maize oil, if properly prepared, is clear in colour, and does not require refining for commercial purposes. If, however, the oil is badly prepared and allowed to stand in contact with albuminoid matter so that it undergoes a process of fermentation, whereby considerable quantities of free fatty acids are produced (see Vol. I. Chap. I.), it acquires a dark colour and would be unsuitable for light-coloured soaps. Such oil is therefore bleached in soap works in the same manner as linseed oil (p. 49).

The freshly-prepared maize oil is of a pale yellow or golden-yellow colour, and has a distinctive odour; its taste is pleasant at first, and is most characteristic in that it resembles that of newly ground corn-meal. It is therefore possible to identify the oil by its taste alone.

The freshly-prepared oil from the germs contains but small quantities of free fatty acids, whereas the oil recovered by the older processes from the fermentation vats was characterised by a large amount of free fatty acids. The solubilities of the oil in absolute alcohol, acetone, and glacial acetic acid, are collated in the following table, due to *Smith* [1] :—

Solubility of Maize Oil in 100 volumes of				
Absolute Alcohol.		Acetone, commercial.	Glacial Acetic Acid.	
At 16° C.	At 63° C.	At 16° C.	At 16° C.	At 63° C.
2	13	24	3	9

Maize oil is characterised by its high amount of unsaponifiable matter. *Spüller* [2] obtained 1·35 per cent, and *Hart* [3] 1·55 per cent, of unsaponifiable matter. *Hopkins* found in a specimen of maize oil 1·49 per cent of lecithin and 1·37 per cent of phytosterol. A sample of maize oil examined in the author's laboratory gave even 2·32 per cent of unsaponifiable matter.

The "unsaponifiable" consists of lecithin, and of an alcohol which was looked upon by earlier observers (*Hoppe-Seyler*, *Hopkins*) as cholesterol. Since, however, purified crystals obtained by *Gill* and *Tufts* [4] from about 4 kilos of maize oil melted at about 138°-138·3° C., the alcohol appears to be phytosterol. The fact that the acetate melted at 127·1° C., and that it seemed to be less soluble in alcohol than the corresponding substance obtained from olive oil, led *Gill* and *Tufts* to the conclusion that the alcohol in the unsaponifiable matter of maize oil is sitosterol and not phytosterol. More recent researches by *Windaus* and *Hauth* having demonstrated that sitosterol and phytosterol are identical, the alcohol in the unsaponifiable matter of

[1] *Journ. Soc. Chem. Ind.* 1892, 505.
[2] *Dingl. Polyt. Journ.* 264, 626.
[3] *Journ. Soc. Chem. Ind.* 1894, 257.
[4] *Journ. Amer. Chem. Soc.* 1903, 251.

maize oil cannot lay claim to an exceptional constitution. *König* and *Schluckebier*[1] repeatedly recrystallised maize oil "phytosterol" and obtained in the sixth, seventh, eighth, and ninth successive crops of crystals the melting points 139·6°, 140·8°, 140·4°, and 140·4° C. respectively. The last crop of crystals was acetylated; the melting point of the acetate in the first crystallisation was 135·8° C. and in the third crystallisation 137° C. In the elaïdin test, maize oil, like cotton seed oil, yields a mass of buttery or pasty consistence. The viscosity of maize oil has been stated by *Winfield* to be at 20° C. 9·79-10·7 times that of water. Taking the viscosity of rape oil at 100, the viscosity of maize oil works out at 70·4-70·65.

The saturated fatty acids in maize oil amount, according to *Hopkins*, to 4·55 per cent; *Tolman* and *Munson*, however, obtained 7·44 per cent of solid fatty acids by the lead-salt-ether method. Hence, *Vulté* and *Gibson's* statement that the mixed fatty acids consist of 27·74 per cent solid fatty acids and 72·26 per cent liquid fatty acids, can only be explained by the fact that the solid acids had not been completely exhausted with ether. This is confirmed by the further statement that the separated solid fatty acids still absorbed 54·23 per cent of iodine.

According to *Vulté* and *Gibson* the solid fatty acids consist of palmitic, stearic, and arachidic acids, but considering that *Hehner* and *Mitchell* found no stearic acid in maize oil, this statement stands in need of confirmation. Amongst the liquid fatty acids linolenic acid seems to be absent, since no ether-insoluble brominated glycerides could be obtained; nor did *Hopkins*[2] find any linusic acid amongst the products of oxidation. Since tetrabromostearic acid was obtained from the liquid fatty acids, the presence of linolic acid is proved. The liquid fatty acid may therefore be considered as consisting of a mixture of linolic and oleic acids. Small quantities of volatile fatty acids occur in the oil, as is evidenced by its high *Reichert* value. Amongst the volatile fatty acids, acetic and formic acids were identified. *Lewkowitsch* found the acetyl value of a sample of maize oil 7·8-8·75: this somewhat high value may be due, to some extent at least, to the large amount of unsaponifiable matter.

Maize oil is, as one would expect from its high iodine value,[3] a representative type of a semi-drying oil; it has somewhat better drying powers than cotton seed oil, but it differs from the latter in that it is not oxidised with equal energy, when finely subdivided on cotton waste, although it "heats" with sufficient rapidity to render it dangerous as a lubricating oil (Vol. III. Chap. XV.). In the *Livache* test two samples of maize oil of different origin gained 5·97 and 5·19 per cent in seven and ten days respectively.[4]

[1] *Zeit. f. Unters. Nahr. u. Genuss.* 1908, xv. 652.

[2] *Journ. Amer. Chem. Soc.* 1899, 948.

[3] *Rokitansky* (*Journ. Chem. Soc.* 1895, Abstr. i. 509) described a maize oil obtained from the yellow Italian maize plant, grown in Southern Russia, as a yellow neutral oil of 0·836 specific gravity, and the (Hübl) iodine number 75·8. These numbers differ so much from those given in the table, that they have not been embodied therein.

[4] H. Winfield, *Dissertation*, New York, 1899.

Physical and Chemical Characteristics of Maize Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9215	Bornemann	−10 to −20	Smith	188-189	Spüller	119·4-119·9	Spüller	0·33	Spüller
,,	0·9244	Smith	−10 to −15	De Negri and Fabris Hopkins Lewkowitsch	193·4	Smith	116·3	Smetham	2·5 [1]	Smith
,,	0·9215-0·9220	De Negri and Fabris	−36 "stearine" deposits at the ordinary temperature on standing		190·4	De Negri and Fabris	122·9	Smith	4·2-4·3	Winfield [2]
,,	0·9239	Hart			189·7	Archbutt	111·2-112·6	De Negri and Fabris		
15·5	0·9274	Lewkowitsch			192·6	Winfield	117	Hart		
,,	0·9243	Archbutt			191·9	Lewkowitsch	121-130 8	Lewkowitsch		
,,	0·9213-0·9255	Winfield					122	Wallenstein		
							121·5-123·1	Hopkins		
100	0·8711-0·8756	,,					122·2-128·02	Williams		

[1] The volatile acids from 108 grms. of oil required 0·56 grms. KOH (*Journ. Soc. Chem. Ind.* 1892, 505).

[2] One sample of "distillery oil" stated to have yielded 88·21 per cent insoluble acids + unsaponifiable, had the high Reichert value of 9·9.

Physical and Chemical Characteristics of Maize Oil—continued

Refractive Index.		Thermal Tests.			
		Maumené Test.		Heat of Bromination.	
At 15·5° C.	Observer.	° C.	Observer.	° C.	Observer.
1·4768	Tolman and Munson	56	Spüller [1]	21·5	Hehner and Mitchell
Butyro-refractometer.		86	De Negri and Fabris [2]		
		89	Smith [3]		
		60·5	Hart [1]		
" Degrees " at 15° C.	Observer.	79	Jean [2]		
		81·6	Archbutt		
77·5	Tolman and Munson				

[1] By Maumené's method. [2] By Jean's method.
[3] 15 grms. of oil and 5 c.c. of sulphuric acid.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	° C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
94·7	Spüller	100	0·8529	Winfield	16-14	De Negri and Fabris	18-20	De Negri and Fabris	198·4	Spüller	125	Spüller
95·7	Hart										113-115	De Negri and Fabris
93·57	Hopkins						20	Jean				
92·2-92·8	Winfield						21·6	Tolman and Munson				
					Titer Test.						Iodine Value of the Liquid Fatty Acids.	
					19	Lewkowitsch					140·7	Wallenstein and Finck
											142·2-143·7[1]	Tortelli and Ruggeri

[1] From an oil having the iodine value 123·3-124·6.

No decided drying properties are imparted to maize oil by subjecting it to the process of "boiling," or by the addition of driers. If, however, a current of air is passed through the oil at 150° C., it acquires, on addition of manganese borate, some drying properties, and a thin film of the oil so treated spread on lead dries in from ten to twenty hours to a viscous mass.

At times when cotton seed oil is lower in price than maize oil, the latter may be adulterated with cotton seed oil. Although it is easy to differentiate maize oil from cotton seed oil, the detection of a small proportion of maize oil in cotton seed oil by chemical tests is at present impossible. *Gill* and *Tufts* are of the opinion that it may be feasible to detect cotton seed oil in maize oil by the melting point of the acetate of the alcohol isolated from the unsaponifiable matter. They obtained from pure cotton seed oil, after recrystallising the acetate six times, crystals of the melting point 120°-121° C.; from a mixture of 90 per cent of cotton seed oil and 10 per cent of maize oil, crystals melting at 121·5°-122·5° C.; and from a mixture of 80 per cent of cotton seed oil and 20 per cent of maize oil, crystals melting at 124°-125° C.; whereas crystals from pure maize oil melted at 127·1° C. Since, however, *Bömer* and *Winter* obtained phytosteryl acetate from cotton seed oil of the melting point 123°-124° C., further confirmation of the reliability of the "sitosterol test" is required. In the present state of our knowledge the *Halphen* colour test (in which the colour of maize oil remains unchanged) and a higher titer test of the fatty acids than 20° C., must be relied upon as indicating the presence of cotton seed oil.

In consequence of the enormous quantities of maize oil that are produced in the United States and in Argentina,[1] and in view of the almost unlimited supply that can be obtained, it is rather to be expected that maize oil will in future be used to adulterate cotton seed oil.

Well-refined maize oil is used for edible purposes (salad oil). Since its "grainy" taste is objectionable, the edible quality is most likely mixed with edible cotton oil and other edible oils. Maize oil is also used in the manufacture of margarine — "oleomargarine" of the United States—as also in the manufacture of compound lard (replacing cotton seed oil). Such maize oil as cannot be employed for edible purposes is used chiefly in making soft soap, for which it is eminently suitable. A cotton "softener" largely used in the United States contains maize oil soft soap. For hard soaps of acceptable quality maize oil is not suitable.

To indicate the extent to which maize oil has been employed in Europe for soap-making, the following statistical data may be quoted :—

[1] It is expected that South Africa will shortly become a large exporter of maize.

[TABLE

Corn Oil—Exports from the United States of America, 1898-1905

Year.	Gallons.	Value. Dollars.
1898	2,646,560	575,646
1899	2,360,623	565,293
1900	4,383,926	1,351,867
1901	4,808,545	1,831,980
1902	4,266,398	1,769,370
1903	3,778,035	1,467,493
1904	3,222,875	998,613
1905	3,108,917	890,937
1906	3,833,251	1,172,206
1907	...	1,083,929

(It is noteworthy that in consequence of the lower prices of cotton oil ruling in the years 1902 and 1903, the import of maize oil into this country almost ceased in those years.) Lower qualities are used as a burning oil. The oil has also been recommended for lubricating, but on account of its gumming properties it cannot be usefully employed for this purpose. Notwithstanding many statements to the contrary, maize oil cannot be used as a paint oil on account of the poor drying properties which paints prepared with this oil possess. It finds, however, extensive employment in the United States for the manufacture of vulcanised maize oil.

PERSIMMON SEED OIL[1]

French—*Huile de plaqueminier de Virginie.* German—*Dattelpflaumenöl.* Italian—*Olio di diospiro.*

For tables of characteristics see p. 136.

This oil was obtained from the seed of *Diospyros virginiana*, L.[2] The oil has a brownish-yellow colour. Its taste and smell resemble that of arachis oil produced in the hot.

The oil is a semi-drying oil. It contains 9·11 per cent of solid acids of the mean molecular weight 298, and 85·5 per cent of liquid acids of the mean molecular weight 285. Amongst the solid acids no arachidic acid could be detected.

[1] N. J. Lane, *Journ. Soc. Chem. Ind.* 1905, 390.

[2] With regard to studies on the ripening of persimmons from the Virginian and Japanese species (*Diospyros Kaki*), cp. Bigelow, Gore, and Howard, *Journ. Amer. Chem. Soc.* 1906, **28**, 688.

Physical and Chemical Characteristics of Persimmon Seed Oil

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
At 15° C.	° C.	° C.	Mgrms. KOH	Per cent.
0·92437	−11	−6	188	116·8

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Specific Gravity.	Solidifying Point.	Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value of Liquid Fatty Acids.
Per cent.	At 15° C.	° C.	° C.	Mgrms. KOH.		
95·9	0·9033	20·2 (Titer Test)	20·2	192·7	291·5	134-135

WHEAT OIL

French—*Huile de blé.* German—*Weizenkernöl.*
Italian—*Olio di germi di grano.*

For tables of characteristics see p. 137.

Wheat oil is contained in the germs of the wheat grains to the extent of 12·5-17·5 per cent (1 to 1·8 per cent of the whole grain). One ton of germs yields about 280 lbs. of oil.[1]

In the fresh state the oil is pale yellow and has the characteristic odour of wheat meal. It is insoluble in anhydrous alcohol in the cold, but dissolves in 30 parts of hot absolute alcohol. At 65° C. it is soluble in an equal volume of glacial acetic acid.

The oil easily turns rancid (most likely owing to the presence of a ferment; cp. "Rice Oil") and thereby becomes dark brown. A freshly extracted specimen contained 5·65 per cent of free fatty acids calculated to oleic acid; after one year the same sample contained 43·86 per cent. Oils from different germs behave differently, as shown by the numbers given in the tables.

The specimen examined by *Frankforter* and *Harding* contained 2 per cent of lecithin and 2·5 per cent of phytosterol. In the opinion of *Frankforter* and *Harding* the alcohol resembles *Reinke* and *Rodwald's* paracholesterol (sitosterol(?)). The high percentage of both lecithin and alcohol shows the relationship of this oil to maize oil. This oil is not identical with wheat meal oil (cp. p. 240).

[1] *Chem. Revue*, 1904, 128.

Physical and Chemical Characteristics of Wheat Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Refractive Index.		
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At ° C.		Observer.
15 „	0·9245 0·9292- 0·9374	De Negri [1] Frankforter and Harding [2]	15 Semi-solid at 0	De Negri Frankforter and Harding	182·81 187·4-190·3	De Negri Frankforter and Harding	115·17 115·64	De Negri Frankforter and Harding	20 30 40	1·48325 1·47936 1·47447	Frankforter and Harding
									Butyro-refractometer. "Degrees."		
										74·5	De Negri

[1] *Journ. Soc. Chem. Ind.* 1898, 1155.

[2] *Ibid.* 1899, 1030.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer	° C.	Observer.	Per cent.	Observer.
29·7	De Negri	39·5	De Negri	123·27	De Negri

DATURA OIL[1]

French—*Huile de datura.* German—*Stechapfelöl, Daturaöl.*
Italian—*Olio di Stramonio.*

The air-dried seeds of *Datura Stramonium*, L. (thorn apple), contain 16·7 per cent of datura oil.

The solid fatty acids of datura oil include palmitic acid, and acids melting at 53°-54° C. and having a molecular weight exceeding 320. The daturic acid, $C_{17}H_{34}O_2$, which *Holde* at first thought to be an acid characteristic of this oil, has been shown later on by him[2] to be a mixture of acids of molecular weight 280 to 291. There appears to be also present in the oil a solid unsaturated acid which is stated to be readily oxidisable.

When heated to 50° C. in a thin layer for thirteen hours, the oil forms a firm skin; at the ordinary temperature it only begins to show signs of drying after 35 days.

The viscosity of the oil in *Engler's* viscosimeter is 9 compared with water at 20° C.

Physical and Chemical Characteristics of Datura Oil

Specific Gravity at 15° C.	Solidifying Point.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9175	thickens at – 15°	186	113

The oil from *Datura metel* which furnishes the so-called metel nuts, known to the natives of East Africa for their medicinal properties, has been described by *F. Suzzi.*[3] The seeds contain 15·27 per cent of a pale yellow oil having a peculiar odour and an unpleasant taste. *Suzzi* gives the following characteristics:—

Oil

Specific gravity at 15° C.	0·9225
Solidifying point	12-15° C.
Saponification value	198·4
Iodine value	116·2
Maumené test	74·8° C.

Fatty Acids

Solidifying point (titer test)	22·3° C.
Neutralisation value	195·1
Saponification value	196
Mean molecular weight	286·2

[1] Holde, *Mitth. d. Königl. Tech. Versuchs.* 1902, 20 [2], 66. Cp. also *ibid.* 1903, 59.
[2] *Berichte*, 1905, 1252.
[3] *I semi oleosi e gli Oli.* Published for the Milan Exhibition, 1906.

The oil gives neither the *Halphen* nor the *Baudouin* test. It is used as a burning oil in Erythrea (Italian East Africa).

BEECHNUT OIL

French—*Huile de faîne.* German—*Bucheckernöl.*
Italian—*Olio di faggio.*

For tables of characteristics see p. 140.

Beechnut oil is obtained from the fruit of the red beech-tree, *Fagus sylvatica*, L. The fruit consists of 33 per cent of husks and 67 per cent of kernels. The latter contain 43 per cent of oil. The oil is prepared in small installations on the Continent, as obviously it cannot be obtained in large quantities. (A patent[1] was taken out in this country as early as 1713 for the manufacture of beechnut oil, but the oil is not produced in this country at present.) The cold-drawn oil obtained from the shelled kernels is of pale yellow colour and free from unpleasant taste. This quality of oil is used for culinary purposes, whereas that expressed at a higher temperature is employed as burning oil.

Beechnut oil is stated to be used as an adulterant of almond oil; its presence may be detected by determining the **iodine value** of the sample.

[1] Aaron Hill, English patent 393, 1713.

Physical and Chemical Characteristics of Beechnut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	"Degrees" at 22° C.	Observer.
0·9225	Schübler	−17	Chateau	196·3	Girard	111·2	De Negri and Fabris	65	Maumené	+16·5 to +18	Jean
0·9205	Massie			191·1	De Negri and Fabris			63	De Negri and Fabris		
0·9220	De Negri and Fabris					120·1	Wijs				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Per cent.	Observer.
95·16	Girard	17	Girard	24	Girard	114	De Negri and Fabris
				23	De Negri and Fabris		

KAPOK OIL

French—*Huile de kapock.* German—*Kapoköl.*
Italian—*Olio di kapok.*

For tables of characteristics see p. 142.

Kapok oil is obtained by expressing the seeds of *Eriodendron anfractuosum*, D.C. (= *Bombax pentandrum*, L.), and *Bombax Ceiba* (= *Bombax malabaricum*, D.C.). Both trees are indigenous to the Tropics. *E. anfractuosum* grows in great profusion in the East and West Indies, the Malayan Archipelago, Indo-China (Cochin-China and Cambodja), Mexico, the Antilles, Guiana, and Africa (Madagascar, Senegal, Ivory Coast, Dahomey, Nigeria). In Nigeria the tree is known as "cotton tree" and "silk cotton tree." The seeds are of the size of peas; they are enclosed in a hard black shell, constituting about 40 per cent of the seeds. The plant is related to the cotton plant, and the hairs covering the fruit resemble cotton, although they have neither the strength nor the staple of the latter.[1]

The seeds are free from hairs, hence they do not offer the same difficulty which cotton seed presents to the seed-crusher. A light crushing between rollers and winnowing through sieves, assisted by a current of air, separates the husk from the kernel. The seed is expressed on a commercial scale in Holland; the yield of the oil from the whole seed is 17·8 per cent on a manufacturing scale, whilst by extraction with ether 24·8 per cent of oil are obtainable.

The oil has a greenish-yellow colour and a not unpleasant taste and odour.

The numbers given in the table of characteristics show very great differences, especially as regards the saponification and iodine values. The great resemblance of this oil to cotton seed oil indicates that the iodine value 75·5 to 68·5 must be accepted with reserve, the iodine value of 117·9 to 119·4 being the more reliable one. On the other hand, *Henriques's* saponification value appears to be too low; the number 196·5, given by *Philippe*, agrees with the percentage of insoluble fatty acids, yet the *Reichert* value stated by *Philippe* cannot be reconciled with both the saponification value and the percentage of insoluble acids + unsaponifiable matter he had ascertained. Again, the high saponification value stated by *Durand* and *Baud* agrees better with the *Reichert* value. The discrepancy in the saponification values, as given by these different observers, may find its explanation in the occurrence of hydroxylated acids, which readily form lactones. This is clearly indicated by the high acetyl value, in conjunction with the remarkably low neutralisation value of the mixed fatty acids found by *Philippe*. The neutralisation value given by *Henriques* seems, however, to exclude the presence of lactonic acids. Renewed examination of the oil is therefore desirable.

[1] *Journ. Soc. Arts*, 1893, 1030; *Journ. Soc. Chem. Ind.* 1894, 147.

Physical and Chemical Characteristics of Kapok Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Maumené Test.		Refractive Index. Oleo-refractometer at 40° C.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	"Degrees."	Observer.
15 18 100	0·9237 0·9199 0·8613	Philippe [1] Henriques [5] Durand and Baud [2]	29·6	Durand and Baud	181 196·5 205·0	Henriques Philippe Durand and Baud	117·9-119·4 75·5 (?) 68·5 (?) 129	Henriques Philippe [1] Durand and Baud (?[4])	3·3	Philippe	95	Henriques [3]	51·3	Durand and Baud

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Acetyl Value.		Iodine Value.	
Per cent.	Observer.	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.		Observer.	Per cent.	Observer.
94·9 95·4	Henriques Philippe	18	0·9162	Henriques	23-24 31·5 32	Henriques Philippe Durand and Baud	29 35·5-36	Henriques Philippe	191 134·6 190	Henriques Philippe (?[4])	293	Henriques	86	Philippe	108 122·5	Henriques (?[4])

[1] *Moniteur Scientifique*, 1902, 728 (the oil was obtained by cold pressing).
[2] *Ann. Chim. anal. appl.* 8, 1903, 328 (the oil was extracted with ether).
[3] By Archbutt's process.
[4] *Chem. Revue*, 1902, 274.
[5] *Journ. Soc. Chem. Ind.* 1894, 258.

The mixed fatty acids consist, according to *Philippe*, of 30 per cent of solid fatty acids, and 70 per cent of liquid fatty acids (determined by the lead-salt-ether method). The solid acids consist exclusively of palmitic acid. On standing, kapok oil, like cotton seed oil, deposits "stearine." The great resemblance of kapok oil to cotton seed oil is further accentuated by the great similarity of the colour reactions of the two oils. Thus kapok oil gives with nitric acid a similar reaction to that which cotton seed oil shows; in the case of kapok oil the tint is stated to be more greenish-brown than reddish-brown. It is also stated that the most characteristic colour reaction of cotton seed oil—the *Halphen* test—is given by kapok oil. This fact deserves attention on the part of the analyst. It should, however, be distinctly noted that a sample of kapok oil extracted by the author from genuine seeds of *Eriodendron anfractuosum* did not exhibit the *Halphen* reaction. Perhaps this may be due to the oil having stood before testing about thirteen months.

Kapok oil is used in its home for edible purposes. Seeds imported from Java are crushed in Holland, and the oil is used for soap-making as a substitute for cotton seed oil. Attempts are being made in Marseilles to crush Kapok seed.

COTTON SEED OIL

French—*Huile de coton.* German—*Baumwollsamenöl, Cottonöl.*
Italian—*Olio di cotone.*

For tables of characteristics see pp. 149-151.

Cotton seed oil is obtained on a very large scale from the seeds of the various kinds of the cotton tree, *Gossypium.* The species cultivated extensively in the United States is *Gossypium hirsutum*, L. ("Upland cotton" covered with "linters"), whereas the plant grown in the Sea Islands and in Egypt is *Gossypium barbadense*, L. During the last decade East India (Bombay) seed, as also Levantine (Smyrna, Mersyne, Alexandretta), Brazilian (Maranhao, Savanilla, Pernambuco), Peruvian (Payta), Russian (Samarkand, Ferghana),[1] and West African (Nigeria) seed has come into the European markets. The Indian species is generally assumed to be *G. neglectum* and *G. arboreum*, but it should be pointed out that the Indian species are not well defined.

The species grown in the Levant are most likely identical with those grown in India. The Brazilian species of *Gossypium* grown in Peru and Brazil is most likely the cultivated species of *G.*

[1] In the Ferghana district the production of cotton seed oil has reached the dimensions of a considerable industry. In the year 1902 there were already six seed-crushing mills. Since then three more mills have been added, producing about 16 tons of oil per day. In the year 1908 there will be opened five more oil mills, intended to produce about 25 tons of oil per day.

peruvianum, Cav.[1] The Brazilian seeds belong to the naked-seeded variety.

In order to show the enormous extent which the cotton seed and cotton seed oil industry [2] has reached during the last thirty years, I append the following table, giving official statistics of the United States of America :—

[1] The author cannot accept any responsibility for the correctness of the botanical species of *Gossypium* assigned above to the different seeds, inasmuch as the highest botanical authorities are at variance with regard to the different species (cp. Todaro, *Relazione sui Cotoni coltivati nel R. orto botanico di Palermo*, Palermo, 1876 ; Wiesner, *Die Rohstoffe des Pflanzenreiches*, vol. ii. p. 233). Recently G. Watt published *The Wild and Cultivated Cotton Seed Plants of the World : A Revision of the Genus Gossypium* ; but "since his classification is based on herbarium species," "numerous errors" have been stated to occur in his work (Fletcher, *Nature*, January 16, 1908). It is, moreover, contended that Watt's classification being based on the presence or absence of a fuzzy covering to the seed below the cotton (such as is found in the "upland" seed of the United States of America and the Indian and Levant seed), must lead to failure, for every cultivated species of cotton comprises the two varieties, viz. one bearing a fuzzy seed and another which bears a naked seed. Thus *Fletcher* has shown that by cultivating fuzzy-seeded American cotton seed in India he has been able to convert it into a naked-seeded variety in a few generations by a simple process of growing it under irrigation in well-manured soil. That such a change occurs is well known to cultivators in the West Indies and other parts of the world. For a vindication of Watt's statements by D. Prain, see *Nature*, February 6, 1908, p. 318.

In view of the discrepancy of opinion amongst botanists, I applied to the Imperial Institute for an authoritative statement. The expert of the Imperial Institute, Mr. E. Goulding, writes as follows :—

"The whole question of the botanical classification of cotton is in a very confused state. This is no doubt mainly due to the cultivation of the plant for extensive periods, and the consequent gradual modification of the distinctive characters of the original species.

"**American Cottons.**—The ordinary **Upland cotton** is fairly generally considered to be derived from *Gossypium hirsutum*, Linn. Some authorities, however, are of opinion that it is derived from *G. herbaceum*, Linn., whilst others regard these two species as identical. In 'The Cotton Plant,' Bulletin No. 33, Office of Experiment Stations, United States Department of Agriculture, the following statement is made on this point —'The weight of opinion seems to be that the species is either *G. herbaceum* or *G. hirsutum*, and as these are considered synonymous, their description is combined under the name of the former.' **Sea Island** cotton has usually been regarded as *G. barbadense*, but is considered by Watt to be a hybrid form.

"**Egyptian Cottons.**—The Egyptian cottons probably cannot be referred to any particular species, but are mostly hybrid forms of *G. barbadense* with other species. Most commonly, Egyptian cottons are regarded as *G. barbadense*, but Watt places them under *G. peruvianum*, Cav., which some authorities consider as synonymous with *G. barbadense*.

"**Indian Cottons.**—With reference to these varieties Professor G. A. Gammie, of the College of Science, Poona, writes in his monograph on 'The Indian Cottons':—'It is clearly evident that we have at the most only one true species of cotton in India, *Gossypium obtusifolium*, with its two sub-species, *G. arboreum* and *G. herbaceum*. Other botanists, however, regard the Indian cottons as derived from various distinct species, including *G. herbaceum*, *G. neglectum*, *G. Wightianum*, and *G. arboreum*.'

"**Brazilian and Peruvian Cottons.**—Brazilian cotton is generally considered to be the product of *G. brasiliense*, Macf., and Peruvian cotton that of *G. peruvianum*, Cav."

[2] The Chinese appear to have been the first to work up cotton seed for oil and cake. The seed was crushed some centuries ago in their native mills ; the oil was burned in their hand lamps and the cake was returned to the land as a valuable fertiliser.

[TABLE

June 30.	Crop.	Seed exported.	Seed worked up.	Oil produced.	Oil-cake [1] produced.	Oil exported.	Oil retained for Home Consumption.
	Tons.	Tons.	Tons.	Gallons.	Tons.	Gallons.	Gallons.
1872	1,317,637	3,180	52,705	2,108,000	18,400	547,165	1,560,835
1873	1,745,145	2,003	52,354	2,094,000	18,300	709,576	1,384,424
1874	1,851,652	3,152	74,066	2,963,000	25,900	782,067	2,180,933
1875	1,686,516	2,658	84,325	3,373,000	29,500	417,387	2,955,613
1876	2,056,746	2,582	123,404	4,936,000	43,200	281,054	4,654,946
1877	1,968,590	5,155	98,429	3,937,000	34,400	1,705,422	2,231,578
1878	2,148,239	8,379	150,376	6,015,000	52,600	4,992,349	1,022,656
1879	2,268,147	8,199	181,451	7,258,000	63,500	5,352,530	1,905,470
1880	2,615,608	6,071	235,404	9,416,000	82,400	6,977,796	2,418,204
1881	3,038,695	5,814	182,321	7,293,000	63,800	3,444,084	3,848,916
1882	2,455,221	5,951	294,626	11,785,000	103,100	713,549	11,071,451
1883	3,266,385	5,900	391,966	15,679,000	137,200	415,611	15,263,389
1884	2,639,498	2,837	395,924	15,837,000	138,500	3,605,946	12,231,054
1885	2,624,835	5,523	498,718	19,949,000	174,500	6,364,279	13,584,721
1886	3,044,544	5,897	578,463	23,138,000	202,400	6,240,139	16,897,861
1887	3,018,360	5,616	694,222	27,769,000	243,000	4,067,138	23,701,862
1888	3,290,871	3,109	822,717	32,909,000	287,900	4,458,597	28,450,403
1889	3,309,564	5,687	794,295	31,772,000	278,000	2,690,700	29,081,300
1890	3,494,811	3,830	873,702	34,948,000	305,800	13,384,385	21,563,615
1891	4,092,678	5,045	1,023,169	40,927,000	358,100	11,003,160	29,923,840
1892	4,273,734	6,075	1,068,433	42,737,000	374,000	13,859,278	28,877,722
1893	3,182,673	2,260	1,050,282	42,011,000	367,600	9,462,074	32,548,926
1894	3,578,613	2,710	1,431,445	57,258,000	501,000	14,958,309	42,299,691
1895	4,792,205	5,526	1,677,271	67,090,840	587,044	21,187,728	45,903,112
1896	3,415,842	13,490	1,434,653	57,386,120	502,128	19,445,848	37,940,272
1897	4,070,100	13,283	1,628,040	65,122,000	569,800	27,198,882	37,923,118
1898	5,252,767	16,382	2,101,106	84,044,000	735,300	40,230,784	43,813,216
1899	5,471,521	17,222	2,352,754	94,110,000	823,400	50,627,219	43,482,781
1900	4,668,346	24,928	2,479,386	93,325,729	884,391	46,902,390	46,423,339
1901	4,830,280	21,665	2,415,140	96,605,600	845,299	49,356,741	47,248,859
1902	4,983,239	28,202	2,975,000	119,000,000	1,041,250	23,042,848	85,957,152
1903	5,208,000	25,811	3,277,233	122,908,158	1,165,339	35,642,994[2]	87,265,164
1904	4,716,591	6,430	3,241,426	121,877,618	1,155,568	29,014,417	92,863,875
1905	6,426,698	10,551	3,345,370	133,817,772	1,360,172	53,345,580	82,282,192
1906	5,060,205	11,859	3,731,175	125,700,928	1,271,740	43,793,519	81,907,409
1907	5,912,646	8,814	3,843,981	175,724,840	1,785,804	41,880,304	133,844,536

[1] Exports of oil-cake since 1895 have been as follows (in tons of 2000 pounds): 1895, 244,858 tons; 1896, 202,468 tons; 1897, 311,693 tons; 1898, 459,863 tons; 1899, 539,996 tons; 1900, 571,852 tons; 1901, 629,343 tons; 1902, 525,233 tons; 1903, 550,196 tons; 1904, 410,175 tons; 1905, 625,954 tons; 1906, 555,417 tons; 1907, 670,484 tons.

[2] Of these there were taken by:—Holland, 6,630,227; France, 5,145,265; Germany, 4,068,121; Mexico, 3,996,840; Great Britain, 2,422,118; Italy, 2,221,140.

According to the Twelfth Census, published by the United States Government, there were in the year ending June 30th, 1900, no less than 369 cotton seed oil mills in operation. In these mills, out of the total amount of seed produced in the year 1899, viz. 4,668,346 tons, a little over half, viz. 2,479,386 tons, were crushed. The several States in which cotton seed oil is grown and crushed are, arranged in the order of their production, the following:— Texas, Georgia, Mississippi, Louisiana, Arkansas, South Carolina, Tennessee, North Carolina, Alabama, Indian Territory, Oklahoma, Missouri, Florida. All the other States together produce less than Florida, whose production is quite insignificant compared with that of Texas.

Comparatively small quantities of American seed are exported, as may be gathered from the table, which states the quantities of cotton seed imported by the United Kingdom during the last six years:—

Cotton Seed imported by the United Kingdom

From	1902.	1903.	1904.	1905.	1906.	1907.
	Tons.	cl[illegible]s.	Tons.	Tons.	Tons.	Tons.
France	1,[illegible]75	712	2,220	978	871	56
Germany	62	476	1,520	1,917	2,314	925
Turkey	12,168	2,381	6,480	8,906	13,753	9,813
Egypt	374,024	313,350	319,077	385,615	362,592	407,797
United States of America	21,241	15,127	4,710	4,132	3,007	1,865
Republic of Colombia	501	302	229	129	193	698
Peru	2,836	2,910	2,137	3,013	3,334	5,088
Chili	768	685	523	622	1,328	576
Brazil	24,061	23,692	18,895	35,092	28,116	28,046
Other foreign countries	984	332	7,604	3,789	2,344	1,435
British East Indies	111,814	176,685	104,230	123,342	202,790	279,288
Other British possessions	688	839	1,028	1,393	1,009[1]	830[2]
Russia	...	...	...	...	229	17,980
Portuguese East India	...	...	...	...	...	13,127
Hayti and San Domingo	...	...	...	...	504	3,253
Total	550,620	537,491	468,653	568,928	624,765	758,152

The bulk of the Egyptian cotton seed comes to England. Thus out of 457,766 tons, shipped from 1st September 1906 to 31st August 1907, 382,542 tons were sent to England. The quantities of Egyptian seed received in the several ports are stated in the following table:—

[1] 400 tons from British West India Islands.
[2] 514 tons from British West India Islands.

	Tons.
Hull	196,282
London	73,335
Liverpool	26,679
Bristol	34,973
Southampton	10,432
Leith	1,901
Sharpness	17,765
Glasgow	3,020
Greenock	2,132
Avonmouth	2,900
Ipswich	2,097
Boston Docks	2,112
Manchester	8,914
Marseilles	21,729
Havre	4,885
Dunkirk	4,983
Nantes	5,490
Bremen	9,398
Rotterdam	6,655
Hamburg	7,459
Lisbon	600
Trieste	8,498
Syria	68
Total	457,766

The re-export of seed from the United Kingdom is quite insignificant; it reaches 350 tons per annum.

The quantity of cotton seed oil exported from the United Kingdom is comparatively small, most of the cotton seed oil being consumed at home. The cotton seed oil exports are detailed in the following tables :—

Cotton Seed Oil exported from the United Kingdom

To	1902.	1903.	1904.
	Tons.	Tons.	Tons.
Norway	...	...	...
Sweden	1,182	771	506
Denmark	131	71	39
Germany	8,356	7,134	3,744
Holland	7,950	6,090	4,585
Belgium	5,506	2,863	2,166
France	1,555	1,551	1,656
Algeria	260	29	161
Austrian territories	1,921	2,486	1,621
Roumania	52	103	10
Egypt	20	272	183
Morocco	63	...	...
Other foreign countries	1,107	1,325	1,748
British possessions	427	423	507
Total	28,530	23,118	16,726 [1]

[1] Included in this figure are Re-exports—1249 tons valued £23,558.

Crude and Refined Cotton Seed Oil Exports and Re-exports from the United Kingdom

Country.	Crude Oil.						Refined Oil.					
	Exports.			Re-exports.			Exports.			Re-exports.		
	1905.	1906.	1907.	1905.	1906.	1907.	1905.	1906.	1907.	1905.	1906.	1907.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Norway	...	...	...	...	...	...	...	...	...	446	35	50
Sweden	522	7	0	...	...	...	...	...	...	253	140	4
Germany	4,210	84	3	...	...	...	728	4,911	3,682	700	900	233
Holland	3,713	0	42	...	...	...	1618	5,294	7,237	...	...	...
Belgium	2,943	5	0	...	...	...	533	4,129	3,871	...	...	...
France	426	7	6	...	...	...	390	7,049	9,781	...	...	...
French West Africa . .	...	...	...	...	...	...	702	1,011	1,197	...	...	...
Egypt	...	...	...	...	...	...	245	173	25	...	...	...
Morocco	...	...	...	...	...	...	513	540	176	...	...	...
Other foreign countries .	774	16	7	59 [1]	208 [1]	134 [1]	456	2,232	2,224	133	116	377
British possessions . .	149	40	12	92	...	...	378	816	622	49	186	154
United States of America .	...	...	...	...	...	...	...	...	...	...	...	901
Total . . .	12,737	159	70	151	208	134	5563	26,155	28,815	1581	1377	1719

[1] Totals to all foreign countries.

Physical and Chemical Characteristics of Cotton Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At ° C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·922-0·930	Allen	3 – 4	Lewkowitsch	191-196·5	Allen	106	Hübl
,,	0·9228	Valenta	Below 12° "stearine" separates out from the oil.		196	Dieterich	108·7	Moore
,,	0·9222	Thomson and Ballantyne			191·6-193·5	Thomson and Ballantyne	106·8-108·3	Thomson and Ballantyne
,,	0·923-0·925	De Negri and Fabris			191·8-193·8	De Negri and Fabris	100·9-116·9 [1]	Wiley
,,	0·923-0·926	Shukoff			192-194·5 [4]	Shukoff	106·9-110	De Negri and Fabris
15·5	0·9250	Lewkowitsch					106·5-108 [2]	Wallenstein and Finck
18	0·9203	Long					106·8 [3]	
,,	0·9230	Stilurell					105-110	Lewkowitsch [1]
99 (water at 15·5 = 1)	0·8725	Allen					106-111	Wijs
							112-116 [4]	Shukoff
100	0·8672	Leone and Longi					? 119·5-120·5 [5]	Lewkowitsch

[1] American oil. [2] Egyptian oil. [3] Peruvian oil. [4] Samarkand oil. [5] Bombay oil.

Physical and Chemical Characteristics of Cotton Seed Oil—continued

Thermal Tests.				Refractive Index.		
Maumené Test.		Heat of Bromination.				
°C.	Observer.	°C.	Observer.	At °C.		Observer.
75-76	Archbutt	19·4	Hehner and Mitchell	15	1·4743-1·4752	Strohmer
74-75	Allen			15·5	1·4737-1·4757	Tolman and Munson
68-70	Del Torre			20	1·4722	Harvey
80-90	Wiley			60	1·4570	Thoerner
50-53	De Negri and Fabris			Oleo-refractometer.		
78	Tortelli[1]			"Degrees" at 22° C.		Observer.
Specific Temperature Reaction.				+20		Jean
169-170	Thomson and Ballantyne			+17 to +23		Pearmain
				Butyro-refractometer.		
				°C.	"Degrees."	Observer.
				15·5	72·3-75·6	Tolman and Munson
				25	67·8	Beckurts and Seiler
				,,	67·6-69·4	Mansfeld
				40	58·4	White

[1] Tortelli's Thermoleometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molec. Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60°C.	Observer.
95·87	Bensemann	15·5 (water at 4=1)	0·92055-0·9219	Crampton	32	Allen	35·2	Allen	203·9	Valenta	275	Valenta	110·9-111·4	Morawski and Demski	1·4460	Thoerner
96·17	Lengfeld and Paparelli				30·5	Hübl	35	Hübl	208	Dieterich			115·7	Williams		
95·9	Lewkowitsch	40 (water at 4=1)	0·90497-0·90612	,,	35	Bach	38	Bach	201·6	Thoerner			112·8-113	De Negri and Fabris		
					36	Dieterich	38·5	Dieterich					112-115	Thoerner		
		50 (water at 4=1)	0·89861-0·89972	,,	39-40	Bensemann [1]	42-43	Bensemann [1]					Iodine Value of the Liquid Fatty Acids.		Refractive Index of the Liquid Fatty Acids.	
					32-35	Thoerner	35-40	Thoerner								
		100 (water at 4=1)	0·86542-0·86774	,,	Titer Test.								147·3-147·5 [4]	Wallenstein and Finck	Butyro-refracto-meter. "Degrees."	
													146·8-148·2 [5]	,,		
													147·8 [6]	Lewkowitsch		
		99 (water at 15·5=1)	0·8467	Allen	32·2-32·7 [2]	Lewkowitsch	34-35	De Negri and Fabris					149 [5]	Bömer		
					33·3-34·1 [2]	,,	35-37	,,					141·9-144·5	Tortelli and Ruggeri	At 48°C.	
		100 (water at 100=1)	0·8816	Archbutt	33·0-33·3 [2]	,,	37-38	,,					148·9-151·7 [7]			
					34·4-35·2 [2]	,,							147·3 [8]		53·7-51·4	Bömer
					33·3-35·0 [2]	,,										
					35·6-37·6 [3]	,,										
					28·1-28·5 [9]	,,										

[1] Determined by Bensemann's method, Vol. I. Chap. V. [2] Part of the "stearine" taken out of the oil. [3] All the "stearine" left in the oil. [4] American oil.
[5] Egyptian oil. [6] Peruvian oil. [7] Iodine value of oil 107·9-110·1. [8] Iodine value of oil 105·3. [9] Winter oil.

The importations of cotton seed into France are stated in the following table :—

Year.	Tons.
1896	30,978
1897	53,016
1898	56,357
1899	45,465
1900	50,125
1901	46,959
1902	44,747
1903	30,158
1904	20,112
1905	35,502
1906	35,540

The French imports and exports of cotton seed oil are summarised in the following table :—

Year.	Imports.	Exports.
	Metric Tons.	Metric Tons.
1896	28,001	483
1897	57,610	1680
1898	66,505	2847
1899	72,830	2868
1900	49,361	1834
1901	42,595	1880
1902	28,337	1425
1903	21,605	1496
1904	23,272	809
1905	42,072	1942
1906	37,429	2288

In Germany cotton seed is expressed especially for the production of cotton seed oil for margarine, and this manufacture is confined to the north of Germany (Bremen, Northern Rhine). The cotton seed is imported from Egypt and from South America (Peru, Brazil). At Trieste cotton seed oil is being produced from Egyptian seed.

During the latter years cotton seed is also crushed in Turkestan ; most of the seedlings of the cotton plant have been imported from Egypt and the United States of America ("upland" seed). All the oil produced in Turkestan is consumed locally.

According to the latest census of the United States Government there were in operation in 1907 the following numbers of cotton seed mills :—United States, 786 ; England, 25 ; Egypt, 7 (consuming about 105,000 tons of seed out of a total production of 750,000 tons) ; India, 1 (consuming about 10,000 tons a year out of a total production of 200,000 tons) ; Russia, 6 ; France, 5 ; Germany, 2 ; Mexico, 4 ; China, 10 ; Peru, 15 ; other South America, 12.

Cotton seed is covered with woolly hairs, yielding the well-known cotton fibre. In the case of Egyptian, Sea Island, and Jamaica cotton seed, this fibre is easily removable by means of suitable delinting

machines, so that the seed can be crushed and pressed without previously removing the husk. In the case of American upland seed, of Smyrna (Levant) seed, and especially of Bombay seed, the cotton fibre so tenaciously adheres to the husk that the usual delinting machines are unable to remove the whole of the hairs; notably in the case of Bombay seed, a fine "down" adheres to the husk. Such seeds are decorticated in decorticating machines ("hullers") before crushing, and the kernels ("meats") are separated from the husks by means of another set of machines ("meats and hull separators"). Chemical processes for removing the "down" are resorted to less frequently. The principle underlying these chemical processes is the same that is made use of in carbonising "union" (wool and cotton) rags.[1] Another process[2] consists in treating with alkalis and molasses and then allowing to ferment; the hulls are stated to separate readily from the kernels.

An examination made in the author's laboratory of various kinds of seeds yielded the following results :—

Oil contained in Cotton Seeds (Lewkowitsch)

Kind of Seed.	Kernels. Per cent.	Husks. Per cent.	Oil from		
			Whole Seed. Per cent.	Kernels. Per cent.	Husks ("Hulls"). Per cent.
I. Maranhao .	58·8	41·2	21·54	36·0	0·9
II. ,, .	59·8	40·2	20·89	34·7	0·4
Coromandel .	...	...	16	...	...
Egyptian (1899) .	60·0	40·0	21·98	37·41	...
,, (1900) .	60·06	40·2	23·93	38·7	0·67
Mersyne . .	44·4	54·8	18·67	37·44	1·2
Bombay . .	51·0	49·0	20·56[3]	39·28	1·08
American Upland	...	...	23·46	...	...
Jamaica . .	60·0	40·0	23·6	39·3	0·37
Peru . . .	...	...	...	35·2	...

It will be seen that the Levantine (Mersyne) seed yields the lowest percentage of oil.[3] In this connection, it is noteworthy that seed of American and Egyptian origin grown at Bokhara contains only 17·5 per cent of oil.

A distinction must be made between decorticated and undecorticated seeds. Undecorticated seeds are chiefly crushed in England, France, and Germany from Egyptian, Bombay, and also Smyrna seeds, whereas the vast majority of the American upland seed is crushed in the decorticated state. Also Bombay seed is decorticated in some establishments before crushing.

The kernels are permeated with cells containing deep brown

[1] Cp. English patent 12,539, 1902. [2] Cp. United States patent 695,476.

[3] This is somewhat high ; the average percentage of Bombay seed is nearer 18 per cent. Cp. Wagner and Clement, *Zeit. Unters. Nahr. u. Genussm.* 1908, xvi. 147.

colouring matter; hence the crude cotton seed oil running from the hydraulic presses has a ruby-red to almost black colour.

Cotton seed cake made from decorticated seed contains as a rule about 5 per cent of oil. The husks which remain in the cake are not detrimental to the cattle as long as the non-fuzzy variety of seed is used. The fuzzy-seeded varieties should not be employed in the undecorticated state for the production of cakes as the small fibres form "balls" in the stomach of the cattle. The "decorticated" cakes are usually ground to meal; in this form cotton meal is largely imported from the United States, especially by the Continent. Such cotton meal usually contains 10 per cent of oil. As this meal is as a rule light-coloured, attempts have been made (especially on the Continent) to "bleach" inferior meal by adding small quantities of borax, etc.

The depth of the colour of crude cotton oil depends, in the first instance, on the state of freshness of the seed. The American seed, which is to a large extent crushed shortly after having been harvested, yields a crude oil of much paler colour than that of crude oil obtained in England, France, and Germany from Egyptian seed. The palest Egyptian or Indian crude oil is obtained from fresh seed. When the seed is stored for several months it undergoes some deterioration ("heating," which may also occur during the voyage); hence the crude oil obtained from Egyptian seed in July and August has the darkest colour.

In the American trade three grades of crude cotton seed oil are recognised, viz. "prime," "choice," and "off" qualities. The following are the recognised definitions of these three grades:—

"*Prime crude* cotton seed oil must be made from sound decorticated seed, must be free from water and foots, and must be sweet in flavour and odour. It should produce prime summer yellow oil when refined with caustic soda, with a loss in weight not exceeding 9 per cent. Should the loss in refining be greater than 9 per cent, but the oil obtained be still of prime summer yellow grade (and it cannot be rejected by the buyer), the price must be reduced by a corresponding amount."

"*Choice crude* oil must be manufactured from sound decorticated seed, must be free from water and foots, sweet in flavour and odour, and should produce by proper methods of refining choice summer yellow oil, with no greater loss in weight than 6 per cent for Texas oil and 7 per cent from oil of other seeds. The percentage of free fatty acids should not exceed 1 per cent (as oleic acid).

"Qualities which correspond to neither of the grades mentioned are termed '*off*' oil, and are sold by sample."

The characteristic test of crude oil is the following:—

On saponifying the crude oil with caustic potash, the upper layers which are exposed to the air become blue and afterwards violet—a very characteristic reaction of crude cotton seed oil. If alkali be used in insufficient quantity to produce complete saponification, the colouring matter is carried down together with the soap formed, so that the supernatant oil is but slightly yellowish.

On this reaction is based the technical method of refining cotton seed oil. The oil is warmed (to 120° F.) and then intimately intermixed with dilute caustic soda solution. The proportion of caustic soda required depends on the quality of the oil; only so much caustic soda should be added as to combine with the colouring matter and the free fatty acids in the oil. Sufficient caustic soda has been added if a sample examined on a glass plate appears "broken." Caustic soda when applied in excess causes saponification, and in that case the whole mass is apt to form a homogeneous mixture, which very frequently refuses to separate into two layers. If a judicious amount of caustic soda has been added, which is generally ascertained in the works laboratory by a small scale test, the mixture will readily separate, on standing, into two layers. The upper layer consists of decolourised oil; the lower one forms a black to light brown heavy liquid ("mucilage"), this being a solution of dark brown colouring matter[1] in the soap resulting from the union of free fatty acids and caustic soda.

The mucilage also contains some neutral oil, which has been mechanically carried down or has been emulsified by the soap solution. The mucilage from fresh oil, especially from American crude oil, is of comparatively light colour. A large quantity of mucilage, especially in America, is, therefore, converted into soap, after removing the bulk of the colouring matter in the soap pan by "cutting" the soap with alkali. The soap so obtained is sold at a low price as "foots soap" (Vol. III. Chap. XVI.). Dark-coloured mucilage is treated with mineral acid, the separated fatty mass is distilled, and the distillate worked up for oleine and stearine (Vol. III. Chap. XVI.).[2] The supernatant oil is then drawn off and washed with warm water. Since alkalies are used in refining cotton seed oil, the fact that commercial cotton seed oil is practically free from fatty acids is readily explained.

The loss in refining depends on the freshness of the oil and the care exercised by the manufacturer. The permissible losses in American crude oil have implicitly been given above. In the United Kingdom the refiners use more care than the American oil millers, and the losses are therefore considerably smaller. The smallest losses are made in November, December, January, February, increasing in the months following owing to old seed being employed.

If the oil be intended for edible purposes it must not be bleached with chemicals, whereas for commercial purposes—"soap oil"—the oil is bleached with bleaching powder and mineral acid, and then washed with water until the mineral acid has been removed completely.

In the American trade three kinds of refined oils are discriminated, viz. "Prime summer yellow," "Choice summer yellow," and "Off summer yellow" oils. *Prime summer yellow* oil is required to be clear,

[1] Experiments have been made repeatedly to recover the brown colouring matter, which has been termed "Gossypol"; all the patented processes having for their object the commercial preparation of the colouring matter have so far ended in failure.

[2] English patent 23,231, 1900 (British Oil and Cake Mills, and A. G. Wass), claims the manufacture of printing ink from mucilage.

free from water and foots, sweet in flavour and odour, and of no deeper colour than 35 parts yellow and 7·1 parts red in *Lovibond's* tintometer. *Choice summer yellow* must be clear, free from moisture, and sweet in flavour and odour. *Off summer yellow* must be free from water and foots, and may be of lower quality as regards taste and colour. The refined oil is graded in the United States according to colour. The Interstate Cotton Seed Crushers' Association has adopted as the standard for grading refined oil *Lovibond's* tintometer. Thus prime summer oil must not have no deeper colour at about 70° F. than the combination of 35 yellow units and 7·1 red units of *Lovibond's* tintometer shows. The oil intended for edible purposes is bleached with fuller's earth (see Chap. XIII.).

Cotton seed oil is suitable for edible purposes, but popular prejudice has largely militated against the edible quality being sold under its true name. Hence, the oil has appeared in the market under the disguise of such names as "table oil," "salad oil," "sweet nut oil," "butter oil," etc. Enormous quantities of the "butter oil" quality are used in the manufacture of margarine and compound lards. The commercial brands "summer oil" and "winter oil" differ in that the winter oil has the bulk of the "stearine" removed, so that the oil should remain fluid, even during the winter. Such winter oil or "demargarinated" oil is characterised by a low titer test. Thus the titer test of a sample of demargarinated oil manufactured by the author on a commercial scale was 28·1°-28·5° C.

Two grades of winter oils are recognised at the New York Produce Exchange: "prime winter white" cotton seed oil, and "prime winter yellow" cotton seed oil. Prime winter white cotton seed oil must be perfectly clear, straw-white to white in colour, sweet in flavour and dry, and must remain clear, at a temperature of 32° F., for five hours. Prime winter yellow cotton seed oil must be transparent, free from water and foots, sweet in flavour and odour, straw-coloured (not reddish), and must remain clear, at a temperature of 32° F., for five hours. The cold test relied upon must be carried out as follows: A 4-oz. sample bottle is filled with the oil, a thermometer inserted through the cork of the bottle, and closed tight. The oil is then warmed slowly to 80° F. and allowed to remain at that temperature fifteen minutes. It is then put into a box surrounded by ice and allowed to stand in the box for five hours. After this time it must still be clear, brilliant, and free from "stearine."

As a by-product of winter oil there is obtained "cotton seed stearine"[1] (French—*Margarine de coton, Margarine végétale.* German—*Baumwollstearin, Vegetabilisches Margarin.* Italian—*Margarina di cotone*), a light-yellow fat of buttery consistence. This cotton seed stearine is manufactured on a large scale, especially in the United States, in the process of producing "winter oil," by cooling cotton seed oil, draining off or filtering off the solid deposit, and pressing the latter.

[1] With the above-described cotton seed stearine there must not be confounded the cotton seed "stearine" obtained by distilling the fatty acids obtained from cotton seed oil "mucilage" (cp. Vol. III. Chap. XVI.).

Since cotton seed stearine forms an article of commerce, and is largely used in the manufacture of lard and butter substitutes, it may be of use to record the physical and chemical characteristics (see tables, pp. 158, 159).

It should be noted that, according to the pressure employed in the manufacture, cotton seed stearine will contain a larger or smaller proportion of liquid glycerides; hence, the great divergence of the solidifying and melting points recorded in the table is easily explained. The behaviour of cotton seed stearine in the colour tests is the same as that of cotton seed oil itself. The same holds good of the chemical composition, with this limitation, however, that the proportion of solid fatty acids is larger than in cotton seed oil. Thus *Hehner* and *Mitchell* found in a sample of cotton seed "stearine" 3·3 per cent of stearic acid.

Recent observations by the author have shown that it is doubtful whether stearic acid does occur in cotton seed oil, inasmuch as it was found that the mixed cotton seed fatty acids are capable of dissolving 5 or more per cent of stearic acid, without it being possible to detect the presence of the added stearic acid with the aid of *Hehner* and *Mitchell's* test. According to *Victor J. Meyer*[1] the "stearic" acid found by this method is most likely arachidic acid, or a mixture of palmitic and arachidic acids, since *Meyer* was unable to detect stearic acid in the methylesters of the cotton seed oil fatty acids when subjecting them to fractional distillation according to *Haller's* method.

According to the amount of "stearine" left in the oil, the proportion of glycerides of solid fatty acids in cotton seed oil will vary; therefore such widely different percentages of solid fatty acids as are stated by *Twitchell*, *Farnsteiner*, *Tolman* and *Munson*, viz. from 22·3 to 32·6 per cent, are readily explained. *Boley* (in the author's laboratory) found in a number of American and Egyptian cotton seed oils proportions of solid fatty acids varying from 20·92 to 24·48 per cent.

The solid fatty acids consist chiefly of palmitic acid; small quantities of arachidic acid appear to be present.

No ether-insoluble bromides having been obtained from cotton seed oil, linolenic acids may be considered absent. The liquid fatty acids seem to consist of oleic and linolic acids only. The proportion of linolic acid in the mixed fatty acids calculated from the isolated linolic tetrabromide was found 18·45 per cent (*Farnsteiner*), and 21 per cent (*Lewkowitsch*). From the liquid fatty acids *Farnsteiner* obtained linolic tetrabromide corresponding to 23·9 per cent linolic acid. From the percentage composition of 23·45 per cent linolic acid and 76·55 per cent oleic acid would follow the calculated iodine value of the liquid fatty acids = 111·5. Since direct experiments (cp. table, p. 151) lead to the approximate iodine value of the liquid fatty acids of 150, the amount of linolic tetrabromide found would appear to be much below the truth, and further experiments are required to explain the discrepancy.

[1] *Chem. Zeit.* 1907, 794.

Physical and Chemical Characteristics of Cotton Seed Stearine

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
15	0·91884	Crampton	31-32·5	Allen	40	Allen	194·6	Hart	89·8	Allen	48	Hart
37·7	0·9115-0·912	Muter	...	...	32·2	Muter	194·8-195·1	Lewkowitsch	93·6	Hart		
40	0·90313	Crampton										
50	0·89671	,,										
99 (water 15·5=1)	0·8684	Allen	...	...	39	Mayer	...	...	88·7	De Negri and Fabris		
100	0·867	Hart	...	...	30-31	Hart						
,,	0·86463	Crampton	16-22	De Negri and Fabris	26-29	De Negri and Fabris	...	...	92·7-92·8	Lewkowitsch		
									99·2-103·8	Schweitzer and Lungwitz		
			Titer Test.									
			16-16·05	Lewkowitsch								
			22	,,								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point. Titer Test.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
95·5	Muter	34·9-35·1	Lewkowitsch	27-30	De Negri and Fabris	94·3	De Negri and Fabris
96·3	Hart	40·8	,, [1]				

The fractional distillation of the methylesters of cotton seed oil fatty acids boiling above 200° C. at 18 mm. pressure gave the results detailed in the following table (*Victor J. Meyer*):—

Fraction.	Boiling Point.	Pressure.	Quantity obtained from 535 Grams of Oil.	Iodine Value.
		mm.	Grams.	
I.	up to 201·5°	16	8	77·13
II.	201·5-204°	16	9	101·19
III.	204 -207·5°	16	20	123·51
IV.	207·5-210·5°	16	83	130·87
V.	210·5-214·5°	16	11	123·83
VI.	above 214·5°	16	2	107·23

The iodine values enumerated in the last column confirm the above-stated opinion that oleic acid and linolic acid only are present amongst the unsaturated fatty acids of cotton seed oil, to the practical exclusion of linolenic acid; for the methylesters of oleic acid and linolic acids have the theoretical iodine values 85·82 and 172·78 respectively.

The acetyl values of various samples of cotton seed oil were found by the author [2] to vary from 7·6 to 18, according to the state of freshness of the oil. There was, however, no strict parallelism noticeable between the amount of total volatile acids and the acetyl value.

Cotton seed oil eminently typifies a semi-drying oil. In the *Livache* test it absorbs 5·9 per cent of oxygen in twenty-four hours. By blowing air through cotton seed oil at a temperature of about 90°-100° oxygen is absorbed, with the formation of a small amount only of oxidised acids, the acetyl value rising at the same time considerably. This is shown in the following table, reproducing some experiments made by the author.[3] (Cp. also "Blown Oils," Chap. XV.)

[1] The author is informed that some cotton seed stearines produced in the United States of America have still higher titer tests.

[2] Lewkowitsch, *Analyst*, 1899, 319.

[3] *Ibid.* 322.

	Specific Gravity at 15·5° C.	Total Volatile Acids per Gram in terms of Milligrams. KOH.	Oxidised Acids. Per cent.	True Acetyl Value.
Cotton seed oil . . .	0·9250	0·1	...	7·6
Cotton seed oil, blown two hours at 120° C. . . .	0·9262	2·88	0·51	11·32
Cotton seed oil, blown four hours at 120° C. . . .	0·9291	2·44	0·87	20·46
Cotton seed oil, blown six hours at 120° C.	0·9350	4·60	0·94	25·4
Cotton seed oil, blown ten hours at 120° C.	0·9346	4·16	1·28	30·84

In the following table are contained the numbers obtained by *Procter* and *Holmes*[1]:—

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0[2]	0·920	1·4745	106·0
3	0·926	1·4745	105·0
6	0·926	1·4746	98·0
9	0·926	1·4750	97·0
12	0·927	1·4751	97·0
15	0·929	1·4752	96·0
18	0·929	1·4757	94·0
21	0·931	1·4758	94·0
24	0·936	1·4759	94·0

The mixed fatty acids do not absorb oxygen as rapidly as does the oil itself. Thus in the *Livache* test, only 0·8 per cent were absorbed, as against 5·9 per cent in the case of the oil from which the fatty acids had been derived.

In the elaïdin test a mass is obtained of pasty and buttery consistence.

Cotton seed oil is readily recognised by the high melting and solidifying points of its fatty acids. This characteristic difference from similar oils renders the identification of cotton seed oil a comparatively easy task. This also greatly facilitates the detection of it in other oils and fats. Thus pure maize oil can be easily distinguished from cotton seed oil by the titer test of its fatty acids. The iodine value of cotton seed oil is also important for purposes of identification, especially so the iodine value of its liquid fatty acids, although the iodine numbers are less characteristic than the solidifying and melting points.

The unsaponifiable matter in cotton seed oil varies from 0·73 to 1·64 per cent, and consists to a great extent of phytosterol, in admixture with non-crystallisable colouring matters. Hence, the

[1] *Journ. Soc. Chem. Ind.* 1905, 1287. [2] Original oil.

characteristic phytosterol crystals can but rarely be isolated in a rapid manner from the unsaponifiable matter. According to *Bömer* and *Winter*[1] the crude phytosterol requires to be recrystallised seven or eight times before the pure substance, melting from 136°-137° C., can be obtained. In the phytosteryl acetate test the unsaponifiable matter yields crystals melting from 123·5°-124° C.

Siegfeld[2] obtained from cotton seed oil 0·972 per cent of crude "phytosterol." On recrystallisation from hot alcohol, a resinous dark yellow substance was found adhering to the glass. This substance was completely insoluble in alcohol. From the first mother liquor crystals of indistinct form separated; these were purified separately. After the first crystallisation they showed well-formed plates, obtruncated at both ends. The melting point after the fifth crystallisation was 92·7°-93·7° C. This substance could not be acetylated. After the usual treatment with acetic anhydride, on recrystallising, laminæ of the same form were obtained; the melting point of these was, after the third crystallisation, 92·6°-93·6° C.

The first crystallisation of the unsaponifiable substance showed no definite form, and was strongly contaminated with oil. The second crystallisation yielded long, hard, brittle needles, which melted after the ninth crystallisation at 121·8°-122·2° C. After treatment with acetic anhydride, the substance yielded exactly the same crystals, and their melting point was, after the second crystallisation, 121·8°-122·8° C.

It was only from the mother liquors of this substance that the phytosterol could be obtained in its characteristic crystals. The melting point of the phytosterol after the fifth crystallisation was 138·8°-139·8° C. The melting point of the acetate after the sixth crystallisation was 131·5°-132·5° C. It would therefore appear that *Bömer's* acetate of the melting point 123·5°-124° C. was a mixture of *Siegfeld's* substance, melting at 121·8°-122·8° C., with a certain amount of the real acetate melting at 131·5°-132·5° C.

Cotton seed oil, being one of the cheapest fatty oils, is hardly liable to adulteration. Still, at times when linseed oil and maize oil are much cheaper than cotton seed oil, admixture with these two oils may occur. Linseed oil will be detected by the higher iodine value of the sample, and notably by the bromide test. The detection of maize oil is a more difficult problem (cp. p. 134).

Edible cotton seed oil is employed in immense quantities as a table oil and in the manufacture of margarine, and besides these legitimate uses, for the adulteration of olive oil, lard, and other edible oils and fats. The detection of cotton seed oil in these oils and fats thus becomes one of the most important objects of fat analysis. It is therefore not surprising that the literature on this subject is very voluminous. A number of colour tests have been recommended

[1] *Zeit. f. Unters. d. Nahrgs. u. Genussm.* 1901, 872.

[2] *Ibid.* 1904, 581. Cp. also König and Schluckebier (*Ibid.* 1908, xv. 653), who give as melting point of frequently recrystallised "phytosterol" 137° and 138° C., and the melting points of third, fourth, and fifth crops of its acetate as 123·6°, 124·8°, and 125·8° C. respectively.

for the identification of cotton seed oil and its detection in other oils. The opinions of various observers as to the value of one or other of these colour tests differ greatly. This divergence of statements is in no small degree due to the difference of age and source of the specimens examined. With regard to the latter, it should be noted that American oils differ somewhat from Egyptian oils in their behaviour to the reagents used for the colour reaction.

The author has examined the various colour reactions proposed, and found most of the older tests useless. Hence, they are omitted here.[1] The few colour tests that will be discussed are certainly of assistance to the analyst, but it should be distinctly understood that colour reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can only be used as a preliminary test, or as a confirmatory test.

The best colour test for the identification of cotton seed oil, and for the detection of it in other oils and fats, provided the cotton seed oil has not been heated, is the **Halphen colour reaction.** This test is carried out in the following manner:—1 to 3 c.c. of the oil is dissolved in an equal volume of amyl alcohol; to this is added 1 to 3 c.c. of carbon bisulphide holding in solution 1 per cent of sulphur (flowers). The test-tube containing the mixture is then immersed in boiling water, and kept therein for some time. The carbon bisulphide evaporates off, and cotton seed oil gives in the course of five to fifteen minutes a deep red colouration. This colour reaction is most characteristic, and it is possible to detect thereby 5 per cent, and even less, of cotton seed oil in admixture with other oils and fats, *e.g.* olive oil or lard. In cases where the proportion of cotton seed oil is small, the test-tube must be kept in the water-bath for twenty to thirty minutes, or preferably in a salt-bath at 105° C.[2] Mixtures of olive and arachis oils containing 1 per cent of cotton seed oil gave in the author's laboratory distinct colourations after twenty-five to thirty minutes.

The ease with which this test can be carried out, and its apparent reliability, have led to an overestimation of this very useful and important reaction; so much so that grave errors may be committed by those who assign to this test an exclusive, or even a paramount, importance. It is altogether unjustifiable to look upon this test, as has been done, as permitting of quantitative interpretation.

It is as yet unknown what substance produces the colour reaction in the *Halphen* test, and all conjectures as to its aldehydic nature or otherwise[3] rest on unfounded assumptions. The chromogenetic substance appears to be present in very small quantities only, and is

[1] Cp. second edition, p. 384.

[2] In order to perform the reaction at a still higher temperature Steinmann (*Schweiz. Wochensch. Chem. und Pharm.* 1901 (**39**) 560 (unnecessarily) proposed to add amyl-alcohol to the Halphen reagent.

[3] Cp. Soltsien, *Zeit. f. öffentl. Chemie*, 1899, 306; Charabot and Marsh, *Bull. Soc. Chim.* 1899, 552; Raikow, *Chem. Zeit.* 1899, 760, 892; 1900, 562, 583; 1902, 10; Gill and Denison, *Journ. Amer. Chem. Soc.* 1902, 397; Kargashew, *Pharm. Journ.* 1905 (**44**) 1229; Rupp, *Zeit. f. Unters. d. Nahrgs. u. Genussm.* 1907, xiii. 74; Petkow, *Zeit. f. öffentl. Chemie*, 1907 (**13**) 21. See also footnote, p. 166.

also retained by cotton seed cake; it has the property of passing into the body fat of pigs and cattle fed with cotton cake. Hence the *Halphen* colour reaction can be obtained with lards, etc., which are absolutely free from admixed cotton seed oil.

It should further be noted that failure to obtain the colour in the *Halphen* test does not prove the absence of cotton seed oil. For the chromogenetic substance is destroyed by heating cotton seed oil to 250° C., or even by keeping it at 200° C. for some prolonged time,[1] or by blowing cotton seed oil with air (*Lewkowitsch*), or treating with fuming hydrochloric acid,[2] sulphurous acid,[3] and chlorine. Cotton seed oil so treated no longer gives the *Halphen* colour reaction. Blown cotton seed oil (Vol. III. "Blown Oils") (and even old rancid oil) cannot therefore be identified by the *Halphen* test.

Hence a negative *Halphen* test in a suspected sample is no conclusive proof of the absence of cotton seed oil. Cotton seed oil fatty acids do not show the colour test as distinctly as the oil itself. Frequently the mixed fatty acids obtained by saponifying cotton seed oil give a very faint red colouration only, or even none at all, most of the colouring matter having either been destroyed or washed away in the process of isolating the mixed acids (*Lewkowitsch*).

Finally *Halphen's* test can no longer be considered as exclusively due to cotton seed oil. Kapok oil and baobab oil[4] give the same colour reaction, and the last-named oil with even greater intensity than cotton seed oil (*Milliau*).

In case a negative *Halphen* test be obtained on examining a sample, and the presence of heated cotton seed oil be suspected, confirmation may in some cases be obtained by the **nitric acid** test. This test is best carried out with nitric acid of 1·375 specific gravity, as the author has ascertained by a number of experiments. A few c.c. of the sample are shaken energetically with an equal measure of nitric acid of the specified gravity, and the sample allowed to stand for some time, up to twenty-four hours. Cotton seed oil gives a coffee-brown colouration which is characteristic of this oil to such an extent that admixtures of 10 to 20 per cent of cotton seed oil to olive oil can be detected in certain cases.[5] But even here great circumspection is necessary, as the coffee-brown colouration given by some specimens of cotton seed oil is not characteristic of all cotton seed oils. Thus the author has met with many American cotton seed oils that give the nitric acid test so faintly that olive oils mixed with 10 per cent of this cotton seed oil showed no coffee-brown colouration. Of importance is the observation the author has made, viz. that a

[1] Oilar (*Amer. Chem. Journ.* 24, 355) states that heating for one hour to 140°-150° C. in a steel pan suffices to nullify the Halphen colour test.

[2] Kühn and Bengen, *Zeit. f. Unters. Nahrgs. u. Genussm.* 1906 (xii.), 149.

[3] Fischer and Peyau, *ibid.* 1905 (ix.), 81.

[4] *Compt. rend.* 139 (1904), 807.

[5] Soltsien (*Chem. Revue*, 1908, 29) raises an objection against this test on the ground that olive and hazelnut oils heated to 250° C. also give a brown colouration. This objection is quite unintelligible, for no manufacturer would heat edible olive and hazelnut oils in order to substitute them for cotton seed oil.

specimen of heated cotton seed oil which no longer gives the *Halphen* test still gives the brown colouration with nitric acid, and that also the fatty acids from this specimen of heated cotton seed oil showed the colouration distinctly. This proves incidentally that there are at least two chromogenetic substances present in cotton seed oil.

The Silver Nitrate Test.—This test was first proposed by *Becchi*, and although it has been persistently condemned by a number of observers, it is still being employed by many chemists; hence a discussion of this test must find a place here. Several years ago the Italian government appointed a special committee to inquire into the value of this test, and according to the report given by *Del Torre*, the following two reagents are required :—

REAGENT I.

Silver nitrate	1·00 grm.
Alcohol, 98 per cent (by volume)	200·0 c.c.
Ether	40·0 c.c.
Nitric acid	0·1 grm.

REAGENT II.

Amyl alcohol	100 c.c.
Colza oil	15 c.c.

The test is carried out as follows :—10 c.c. of the oil under examination are mixed in a test tube with 1 c.c. of reagent I., and then shaken with 10 c.c. of reagent II. The mixture is next divided into two equal portions, one of which is put aside for comparison later on, whereas the other is immersed in boiling water for a quarter of an hour. The heated sample is then removed from the water-bath and its colour compared with that of the first portion. Presence of cotton seed oil is indicated by the reddish-brown colouration of the heated portion. *De Negri* and *Fabris* lay stress on the necessity of using the purest alcohol. The colza oil used should be "cold-drawn" oil, and only slightly coloured; it should be filtered in a hot water oven before preparing the reagent. To guard against possible errors arising from the impurity of the reagents a blank test should be instituted side by side with the actual test.

Peruzzi, *Ridolfi*, *Roster*, and *Wiley* have tested *Becchi's* method in the case of over 200 samples of cotton seed oil, and have found it thoroughly reliable, no other oil giving the brown colouration. *Holde*,[1] on the contrary, considers the test as absolutely valueless; but the experiments of *De Negri* and *Fabris*, as also tests made repeatedly by the author (see below), prove that *Holde's* statements are too sweeping, having most likely been deduced from observations on the particular sample he examined.

The *Becchi* test is too capricious to be recommended, Moreover, it is difficult to understand why colza oil is introduced; frequently even serious errors are thereby caused.

[1] *Journ. Soc. Chem. Ind.* 1892, 637.

The statements contained in the literature on *Becchi's* test are of a most conflicting nature.

Benedikt found that some samples of cotton seed oil do not reduce *Becchi's* reagent either with or without the addition of colza oil. Since *Becchi* himself states that old samples of cotton seed oil only reduce the silver nitrate when colza oil has been added, the value of all the modifications proposed becomes doubtful.[1] The author examined mixtures of Egyptian cotton seed oil with olive oil, and finds that an admixture of 10 per cent of cotton seed oil can be detected with certainty, whereas in the case of 5 per cent the reaction becomes indistinct. The silver nitrate test can, therefore, only be relied upon as decidedly indicating the presence of cotton seed oil if a positive reaction has been obtained. Absence of colouration, however, does not prove absence of cotton seed oil. Since even pure lard (see "Lard"), as *Wesson* stated, gives a slight colouration with silver nitrate, and furthermore, as olive oils are often met with which give the *Becchi* reaction to a very marked extent (*Milliau*), even the appearance of a brown colour should not be considered as absolute proof of adulteration with cotton seed oil.

Milliau modifies *Becchi's* test by adding the silver solution to the **mixed fatty acids** instead of to the neutral oil.

Milliau[2] proceeds as follows:—5 c.c. of the fatty acids of the sample are dissolved in 15 c.c. of 95 per cent alcohol, and heated in a water-bath to 90° C. Two c.c. of a 30 per cent solution of silver nitrate are then added, and the mixture is again heated until about one-third of the alcohol has evaporated. If the sample be cotton seed oil, or contain cotton seed oil, the silver nitrate is reduced to metallic silver, producing a black or brown colour in the liquid, or giving particles of reduced silver. Even 1 per cent of cotton seed oil, as *Milliau* states, can thus be detected. *Wiley*[3] considers this test a very useful one, whereas *Hehner*[4] sees no advantage in this modification of *Becchi's* test, an opinion in which the author fully concurs. In many samples, where cotton seed oil was present and was indicated by *Becchi's* test, I could not obtain the reaction.

This fact is explained by an observation made by a French Committee, consisting of *Muntz*, *Durand*, and *Milliau*, viz. that by washing the free fatty acids repeatedly, the substances (supposed to be of an aldehydic nature) which produce the colour reactions are washed away. They therefore recommended not to melt the fatty acids, so as to retain the chromogenetic substance in the mixed fatty acids. *Milliau* proceeds in the following manner:—

15 c.c. of the oil are saponified in a 250 c.c. porcelain dish with alcoholic potash, and the soap is dissolved in 150 c.c. of distilled water. The alcohol is evaporated off by boiling, and the fatty acids are liberated by adding a slight excess of dilute sulphuric acid. The

[1] Wilson also (*Chem. News*, 59, 99) states that cotton seed oil, after keeping for some time, loses its power of reducing silver nitrate.

[2] *Compt. rend.* 106, 550; *Journ. Soc. Chem. Ind.* 1893, 716.

[3] *Lard and Lard Adulterations.* Washington, 1889, 467.

[4] *Analyst*, 13, 165.

solution must not be boiled in order to melt the separated fatty acids, as otherwise the aldehydic substances may pass into the aqueous solution. The emulsified acids are taken off and washed in a wide test tube three times each with 10 c.c. of cold distilled water. Finally, the fatty acids are dissolved in 15 c.c. of 92 per cent alcohol, and 2 c.c. of a 3 per cent silver nitrate solution are added. The test tube is placed, protected from light, in a water-bath and heated to 90° C. until one-third of the alcohol has evaporated off. Ten c.c. of hot distilled water are then added, and the heating continued for a few minutes. In the presence of cotton oil, the fatty acids which float on the top are black, owing to the separation of metallic silver. If the proportion of cotton seed oil exceeds 15 per cent, the aqueous solution is also coloured.

Jean's proposal, viz. to decompose the soap solution obtained on saponifying the oil under petroleum ether, is preferable. The fatty acids, as they are liberated, pass into the petroleum ether, carrying with them the chromogenetic substance; when the petroleum ether solution is subsequently washed, the chromogenetic substance is not removed.

The reduction of silver nitrate is stated to be effected by a substance of an aldehydic nature, the properties of which have not yet been investigated.[1] It should be noted that the silver reducing substance is destroyed or oxidised by heating cotton seed oil or its fatty acids to 240° C. (*Wesson*), or even by keeping the sample or the free acids for some time. Therefore, cotton seed oil heated to 240° C. cannot be identified or recognised in other fats by *Becchi's* or *Milliau's* tests.

Tortelli and *Ruggeri*[2] state that the *Milliau* test becomes more delicate on examining the liquid fatty acids in the following manner:—5 grms. of the liquid fatty acids of the suspected sample are dissolved in 10 c.c. of alcohol, and 1 c.c. of a 5 per cent silver nitrate solution is added; the sample is then heated on a water-bath to 70°-80° C. Cotton seed oil reduces the silver immediately, whereas olive oil and other oils remain clear for some time. Even cotton seed oils—which had been heated to 250° C. for ten and twenty minutes respectively—could be recognised when present in as low a proportion as 10 per cent in olive oil, on allowing the liquid fatty acids of the mixed oil to stand in the hot water-bath for several hours.

From the foregoing remarks it is obvious that the colour reactions can only be used as subsidiary, or at best as confirmatory tests, and

[1] Dupont (*Bull. Soc. Chem.* 1895 [3] 696; *Bull. Chem.* 1895, 811) ascribes the *Becchi* reaction to the formation of silver sulphide, he having obtained on passing a current of steam through cotton seed oil a volatile substance yielding sulphuric acid on oxidation. But as the remaining oil still gave the *Becchi* test, proof for *Dupont's* opinion is wanting. Raikow (*Chem. Zeit.* 1899, pp. 769-802) did not obtain the volatile sulphurised substance, but its occurrence is confirmed by Fischer and Peyau (*Zeit. f. Unters. Nahrgs. u. Genussm.* 1905 (ix.), 81).

[2] *Annali del Laborat. Centr. delle Gabelle*, 1900.

that the *Halphen* test should be supplemented in the case of heated oils by the nitric acid test or by the modified *Milliau's* test suggested by *Tortelli* and *Ruggeri*. The main attention of the analyst should be directed to the indications furnished by the iodine value of the oil (or its mixed fatty acids), the iodine value of the liquid fatty acids, and the solidifying and melting points of the mixed fatty acids. In case an animal oil or fat is suspected of being adulterated with cotton seed oil, the examination of the unsaponifiable matter by the phytosteryl acetate test should not be omitted. Further information on the detection of cotton seed oil will be given under the headings of "Olive Oil," "Lard," and "Tallow," in this chapter; and under "Edible Oils and Fats" in Vol. III. Chapter XV.

It has been pointed out already that the finer grades of cotton seed oil are used for edible purposes.[1] The lower grades are employed in enormous quantities as a soap-making oil. On account of its drying and gumming properties cotton seed oil cannot be recommended as a lubricating oil. It is stated that the blown cotton seed oil (see Vol. III. Chap. XV.) is suitable for lubricating purposes; at any rate considerable quantities of cotton seed oil are converted into blown oil (one brand of such oil is known in the trade as "lardine"[2]). Smaller quantities of cotton seed oil are used as burning oils and in the adulteration of paint oils.

SESAMÉ OIL, BENISEED OIL, GINGELLI OIL, TEEL OIL

French—*Huile de sésame.* German—*Sesamöl.*
Italian—*Olio di sesamo.*

For tables of characteristics see pp. 173, 174.

Sesamé oil is obtained from the seeds of the sesamé plant, belonging to the family of *Bignoniaceæ*. The original home of *Sesamum indicum* is unknown. According to *A. de Candolle* sesamé seed was brought from the Sunda Islands to India several thousand years ago, and has migrated thence through the Euphrates basin to Egypt.

Linnæus differentiated two species, viz. *Sesamum indicum*, L., which produces white or yellow seeds, and *Sesamum orientale*, L., which produces dark (red, brown, or black) seeds. *De Candolle* united the two species of *Linnæus* into one, viz. *Sesamum indicum*, of which he discerns three sub-species, viz.: (1) *S. quadridentatum* = *S. indicum*, L.; (2) *S. subdentatum* = *S. indicum*, Sims; and (3) *S. subindivisum* = *S. orientale*, L.

India produces the largest amount of varieties; there the white seed, yielding the best Indian oil, is termed *suffet-til*, whilst the black

[1] Such oil has been recommended as a basis for ointments in place of lard ("Adeps gossypii").

[2] Not to be confounded with the edible fat "lardine" (see Vol. III. Chap. XV.).

variety, containing the largest proportion of oil, is known as *tillie*. In the trade a mixture of white and dark seeds bears the name *bigarré*.

According to the rules of the trade, the white sesamé must contain at least 85 per cent of white seeds. If the proportion of dark seed exceeds 15 per cent, an allowance is made. If the dark seed exceeds 25 per cent, the term white sesamé seeds no longer applies.

The *bigarré* quality must contain at least 35 per cent of white seeds. The commercial seed known as "*grosses graines*" must not contain more than 20 per cent of "*petites graines*." No more than a maximum of 50 per cent of small seeds is permitted; if they make up from 20 per cent to 50 per cent, an allowance must be made.

By far the largest quantity of *Sesamum indicum* is grown in East India, Java, Siam, Tonkin, China, and Japan. Large quantities are also grown in the countries bordering the Mediterranean, especially in the Levant and Egypt. The seed grown in Africa belongs to the species *Sesamum radiatum*, Shum and Thonn.

Smaller quantities are produced in Algeria and the West Coast of Africa, as also on the East Coast (Mozambique, Zanzibar, German East Africa). In South Rhodesia the seed is cultivated by the natives; it is not unlikely that in the near future it may be exported to Europe.

In South America the plants are grown in Brazil and Venezuela. In the southern states of North America, and in several islands in the West Indies, the cultivation of the plant appears to be on the increase.

Marseilles has become one of the chief emporia for the production of all grades of sesamé oil from the Levant, the Indies, and West Africa. (It is noteworthy that the first Indian seeds from Bombay were imported into Marseilles by *Schloesing Frères* in the year 1879.) The following table giving the imports of sesamé seed into Marseilles shows the growth of this industry :—

	Kilogs.
1834 . .	601
1835 . .	632
1841 . .	1,608,200
1842 . .	12,408,400
1843 . .	17,963,400
1850 . .	25,729,500
1855 . .	34,021,500, of which 15,970,300 from Levant, and 19,051,200 from the "Indies."
1870 . .	77,803,000, of which 12,878,000 from Levant, and 64,925,000 from the "Indies."

The average import during 1901-5 amounted to 79,231,400 kilogs. The highest figure, viz. 123,239,000 kilogs., was reached in 1903, whilst in 1905 the import amounted to 45,050,600 kilogs. only.

The following tables specify the imports of sesamé seed into

France and Marseilles from the Levant, India, and China. The totals include the seed from West Africa :—

Imports of Sesamé Seed into France and Marseilles

France. Metric tons

Year.	The Levant.	India.	China.	Total.
1896	12,037	72,083	97	86,157
1897	14,427	36,656	...	54,227
1898	7,676	60,408	...	68,674
1899	3,775	71,728	893	76,826
1900	6,768	56,660	5,384	69,689
1901	5,531	61,353	4,899	73,791
1902	5,467	65,188	10,670	83,413
1903	3,375	124,453	7,920	138,266
1904	4,497	96,175	...	101,647
1905	3,357	48,198	2,666	55,172
1906	6,877	30,708	20,991	61,194
1907	4,898	59,390	...	68,502

Marseilles. Metric tons

Year.	The Levant.	India.	China.	Total.
1896	11,416	62,568	97	76,021
1897	12,843	33,475	...	49,411
1898	7,236	53,802	...	61,627
1899	3,755	64,013	893	66,090
1900	6,618	53,185	4,834	65,462
1901	4,555	54,454	4,899	65,573
1902	5,108	56,357	9,898	73,367
1903	3,375	110,782	6,649	123,324
1904	4,497	88,770	...	94,225
1905	3,255	44,097	2,512	50,814
1906	6,777	28,213	10,171	57,781
1907	4,485	54,959	2,575	63,561

Other statistics show the exports from the East Indies, China, and German East Africa, calculated by the author to cwts. (1 cwt. = 50·8 kilogs.).

Exports of Sesamé Seed from the East Indies, China, German East Africa, and the Levant

Year.	From		
	East Indies.	China.	German East Africa.
	Kilogs.	Kilogs.	Kilogs.
1891	1,846,732	...	...
1892	2,302,172	...	20,830
1893	2,554,768	...	14,750
1894	2,424,280	138,040	24,357
1895	2,324,793	237,680	22,420
1896	1,800,000	40,094	14,430
1897	1,590,000	53,767	30,621
1898	2,674,700	...	
1899	...	...	
1900	...	...	
1901	...	...	
1902	...	...	
1903	...	631,119	
1904	...	154,880	
1905			
1906			

The sesamé oil industry has not been able to obtain a foothold in Great Britain, inasmuch as the finer qualities of sesamé oil which are obtained in the first expression do not find so remunerative an outlet as they do in other countries; in fact, the whole of the oil would have to be disposed of as soap oil.

The small amount of seed imported into this country is used in the manufacture of compound cake, the high proportion of oil in sesamé seed helping to bring up the percentage of oil in the mixed meal to the legally prescribed amount.

Since the admixture of sesamé oil to margarine has become obligatory in Germany, Austria, and Belgium, a considerable sesamé oil industry has rapidly sprung up in these countries. The figures for Germany and Austria are given in the following tables :—

[TABLE

Imports of Sesamé Seed into Germany

Year.	Total.	From			
		East Indies.	China.	East Africa.	The Levant.
	Double cwts.	Double cwts.	Double cwts.	Double cwts.	Double cwts.
1896	232,530	187,910	...	...	28,570
1897	210,240	186,740	...	...	10,120
1898	312,330	267,470	...	..	24,520
1899	387,710	364,180	...	...	8,900
1900	296,370	261,030	14,410	1131	8,485
1901	358,700	309,950	14,930	3945	21,128
1902	498,180	373,120	91,560	4537	11,228
1903	615,380	427,160	166,730	2234	3,612
1904	513,130	469,960	15,790	5416	16,252
1905	464,892	334,700	...	...	...
1906	573,810	319,380	202,300	...	42,540
1907	668,250	581,108	47,510	...	33,110

Imports of Sesamé Seed into Austria

Year	Kilogs.
1896	8,369,800
1897	7,611,400
1898	13,600,700
1899	12,603,200
1900	13,288,500
1901	15,439,900
1902	12,608,200
1903	31,793,300
1904	36,767,400
1905	15,491,400
1907	19,520,100

Sesamé seed belongs to that class which is rich in oil, and must therefore be subjected to repeated expressions. The proportion of oil varies from 50 to 57 per cent. From the following table, due to *Sprinkmeyer* and *Wagner*,[1] it would appear that African seed contains more oil than Indian, but a much more extended series of experiments is required to justify general conclusions. The table proves further the correctness of the general experience that ether extracts larger quantities of oil from the seeds than does petroleum ether.

Extracted with	Indian Seed.	Levant Seed.	African Seed.
	Per cent.	Per cent.	Per cent.
Ether . . .	49·76	50·14	54·14
Petroleum ether .	47·57	47·57	52·54

[1] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1905 (x.), 353.

The following table gives the *practical yields* obtained on a large scale by the expression of seeds from various countries. The seeds were expressed once or twice in the cold, and then once in the hot.

Practical Yields from Sesamé Seed

Description of Seed.	Per cent.
Bombay seed, yellow or red .	44-45
Bombay seed, bigarré . .	42-44
Levant seed	47-48
Chinese seed	44-45

The oils of the first expression in the cold represent the best qualities.

The finest edible sesamé oil is obtained from the Levant seeds. Of these the Jaffa district yields the best brand. Slightly inferior in flavour to the Jaffa oil are those obtained from seed grown in Caïffa, St. Jean d'Acre, Tarsus, Smyrna, Mersyna. The oil from Alexandretta seeds represents a lower grade still. The Indian seeds, embracing chiefly those from Kurrachee and Bombay, give oils of more unpleasant flavour, and are therefore not usable for the *best kinds* of margarine. Lower still as regards taste and flavour rank the oils from Chinese [1] and African seeds.

The oils of second and third expression are used for manufacturing purposes, chiefly for soap-making.

The press cakes contain from 8 to 10 per cent of oil; they form an excellent cattle food, and are largely in demand for this purpose.

When the seed does not arrive in the sound state in which it is obtained at present almost regularly, the cakes resulting from such unsound seeds are unsuitable [2] for feeding cattle, and are therefore extracted with solvents for the complete recovery of the oil. The extracted meal is then sold as a manure, greatly appreciated by the farmer on account of its fertilising properties. *Bang* and *Sanguinetti* of Marseilles [3] devised a special apparatus for the extraction of sesamé seed with petroleum ether. At present, damaged seed is extracted with carbon bisulphide. In 1903 about twenty million kilograms of press cakes were thus extracted in Marseilles, yielding about two million kilograms of oil. In 1905 only twelve million kilograms of cakes, yielding about one million kilograms of oil, were extracted. The oil so obtained is white or dirty grey. At the ordinary temperature some "stearine" deposits, so that the extracted sesamé oil represents a more or less pasty mass. Owing to the damaged state of the seed the oil contains, of course, a notable proportion of free fatty acids. For the manufacture of mottled soaps the extracted oil can be used as such. If intended to be used as burning oil or for lubricating purposes, the free fatty acids must be removed first.

[1] In China the seeds are roasted before being ground and expressed in wedge presses. Owing to this process the oil becomes dark-coloured and acquires a strong flavour of nuts.

[2] Possibly it is to such unsound seed that the poisonous properties of some sesamé oils, noticed recently (No. 43 *Berliner Klinische Wochenschrift*, 1906), must be ascribed.

[3] Austrian patent, 5th July 1883.

Physical and Chemical Characteristics of Sesamé Oil

Specific Gravity.

At °C.		Observer.
15	0·9230-0·9237	De Negri and Fabris
15	0·924-0·926	Shukoff[1]
15·5	0·9203	Boley[2]
18	0·9208-0·9212	Long
20	0·9170-0·9210	Wijs[3]
23	0·919	Dieterich
35	0·9078-0·9098	Long

Solidifying Point.

°C.	Observer.
−5	Girard
−4 to −6	De Negri and Fabris

Saponification Value.

Mgrms. KOH.	Observer.
194·6	Longi and Leone
187·6-191·6	Filsinger
188·5-190·4	De Negri and Fabris
192-193	Thoerner
188-190	Shukoff[1]

Iodine Value.

Per cent.	Observer.
106	Hübl
108-111·7	Dieterich
106·4-109	Filsinger
107-112	Peters
106·9-107·8	De Negri and Fabris
105-107	Oliveri
103-105	Thoerner
114-115	Shukoff[1]
106·1-114·5	Wijs[5]
105·2-110·3	Wijs[6]
103·9-109·8	Wijs[7]
114[4]	Sprinkmeyer and Wagner
104·2[9]	Suzzi
108-9[10]	,,

Reichert Value.

c.c. $\frac{1}{10}$ norm. KOH.	Observer.
0·35	Medicus and Scherer

Reichert-Meissl Value.

1·2	Thoerner

Thermal Tests.

Maumené Test.

°C.	Observer.
65	Archbutt
63-64	De Negri and Fabris
70[9]	Suzzi
72[10]	,,

Heat of Bromination.

°C.	Observer.
23-23·9	Bromwell and Meyer

Refractive Index.

At °C.		Observer.
15	1·4748-1·4762	Strohmer
20	1·4728	Harvey
60	1·4561	Thoerner

Oleo-refractometer.

"Degrees."	Observer.
+17 to +18	Jean
+13 to +17 at 22° C.	Pearmain

Butyro-refractometer.

At °C.	"Degrees."	Observer.
25	68-68·2[8]	Sprinkmeyer and Wagner
25	69·2[4]	,,
40	59·6-60[8]	,,
40	60·6[4]	,,

[1] Russian oils. [2] Finest Jaffa oil, determined in the author's laboratory. [3] One specimen (from Curaçao seed) had the specific gravity 0·9210.
[4] African oil. [5] One specimen (from Curaçao seed) had the iodine value 116·8. [6] Oils of second expression.
[7] Oils of third expression. [8] Indian and Levant oils.
[9] Oil from Erythrean (Italian East Africa) "bigarré" seed. [10] Oil from Erythrean (Italian East Africa) white seed.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·86	Bensemann	22·3	Hübl	26	Hübl	199·3	Valenta	286	Valenta	108·9-111·4	Morawski and Demski	1·4461	Thoerner
95·6	Dietzell and Kressner	28·5	Dieterich	31·5	Dieterich	201·6	Thoerner			111·8-112	De Negri and Fabris	Butyro-refractometer.	
		18·5	Allen	23	Allen	196·0[7]	Suzzi			110-111	Thoerner		
		25-26	Bensemann[1]	29-30	Bensemann[2]							°C.	"Degrees."	Observer.
		20-22	De Negri and Fabris	21-30	Peters					Liquid Fatty Acids.		25	53·2-54	Utz
		23·5	Thoerner	24-26	De Negri and Fabris					139·9	Lane	40	45·1-47·2	,,
		Titer Test.		25-32	Thoerner					130·9-136·3[3]	Tortelli and Ruggeri	25	55·4-56·5	Sprinkmeyer & Wagner
		22·9-23·55	Lewkowitsch							129·4[4]	,,	,,	54-55[6]	,,
		23·7-23·8	,,							129·5	Lewkowitsch	40	47·2-47·7[5]	,,
		21·2-22·93	,,									,,	45·5-46·8[6]	,,

[1] Point of incipient fusion.
[2] Point of complete fusion.
[3] Iodine value of oil, 108·6-113·7.
[4] Jaffa oil ; iodine value of oil, 109·5.
[5] African oil.
[6] Indian and Levant oils.
[7] Saponification, 198·3.

Sesamé oil contains, according to *Farnsteiner*, 12·1 per cent to 14·1 per cent of solid acids; *Lane*[1] obtained by the lead-salt-ether method 78·1 per cent liquid fatty acids. These consist of oleic and linolic acids. Direct determination of linolic acid (by means of the linolic tetrabromide) gave 16·4, 15·2, and 12·6 per cent linolic acid. From the composition of 12·1 per cent solid acids, 15·8 per cent linolic acid, and 72·1 per cent of oleic acid, there would be calculated as the iodine value of the mixed fatty acids 93·6, whereas direct determination gave the mean value of 111. According to the above-given composition the liquid fatty acids would consist of 82 per cent of oleic acid, and 18 per cent linolic acid. This would lead to 106·4 as the calculated iodine value of the liquid fatty acids, whereas direct determinations have given the mean figure of 133. Also this calculation (cp. "Cotton Seed Oil") shows that the linolic tetrabromide cannot have been fully recovered.

Sesamé oil is dextro-rotatory, a property which may supply a useful additional means of identifying the oil. The numbers ascertained by *Bishop* have been given above (Vol. I. Chap. V.). *Utz*[2] determined the rotations of three specimens of African, Indian, and Levant oils in a 200 mm. tube at 15° C. and found the respective rotations + 1·6°, + 1·4°, and + 0·8°. *Sprinkmeyer* and *Wagner* confirm that the African oil has the highest rotation, whereas they find the lowest rotations in Indian oils. It should, however, be noted that only in the absence of castor, croton, and rosin oils would the polarimetric observation be of any use. The optical activity of the oil is no doubt due to the presence of phytosterol and sesamin (see below).

The amount of unsaponifiable matter in sesamé oil varies from 0·95 per cent to 1·32 per cent. The unsaponifiable matter contains phytosterol, sesamin, and a so-called red oil (see below). The phytosterol was identified by the melting point of the crystals obtained by crystallising it seven times from alcohol. *Siegfeld*[3] thus prepared a phytosterol of the melting point 139·0 – 139·2° C. The phytosterol acetate obtained by *Bömer* from the phytosterol had the melting point 128°-129° C. *Siegfeld* prepared crystals melting at 130-131° C. by recrystallising the acetate seven times. According to *Tocher*[4] glacial acetic acid extracts from sesamé oil two substances—

(*a*) A resinous substance which forms long crystalline needles (from alcohol), melting at 118° C. From a number of ultimate analyses and from determinations of the molecular weight (by *Raoult's* method in benzene and acetic acid) the formula $C_{18}H_{18}O_5$ was derived. This substance was named *sesamin*. Sesamin does not give the *Baudouin* test (see below), but assumes a green and then bright red

[1] *Journ. Soc. Chem. Ind.* 1901, 1083.
[2] *Pharm. Zeit.* 45, 490; *Journ. Soc. Chem. Ind.* 1900, 914.
[3] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1904, 585.
[4] *Pharm. Journ. and Trans.* 1891, 639; 1893, 700.

colour with nitro-sulphuric acid (the colour reaction given by the U.S. Pharmacopœia for sesamé oil).

(*b*) A thick brown oil (of unknown composition) which gives the characteristic colour reactions of sesamé oil.[1]

Villavecchia and *Fabris*[2] state that by extracting the oil itself with either acetic acid or alcohol the chromogenetic substance cannot be wholly removed. By converting the oil into barium soap, and extracting the latter with alcohol, these chemists isolated from the alcoholic extract, by evaporating off the alcohol, and dissolving the residue in petroleum ether, three substances—

1. A higher alcohol of the melting point 137° C., and rotatory power $[a]_D^{20} = -34° 23'$ (for $c = 5{\cdot}013$). This alcohol is doubtless phytosterol.

2. A substance forming fine crystals of the formula $(C_{11}H_{12}O_3)_2$, melting point 123° C. (*Villavecchia* and *Fabris*); $C_{33}H_{30}O_{10}$, melting point 122·5° C. (*Bömer* and *Winter*). Its rotatory power is $[a]_D = +68{\cdot}36$ (for $c = 24{\cdot}45$) in chloroformic solution. This substance was termed *sesamin* by *Villavecchia* and *Fabris*. It is apparently identical with *Tocher's* sesamin $C_{18}H_{18}O_5$, for theory requires for $C_{18}H_{18}O_5$, C = 68·79 per cent, H = 5·73; and for $C_{11}H_{12}O_3$, C = 68·75, H = 6·25; and for $C_{33}H_{30}O_{10}$, C = 67·54 per cent, H = 5·17 per cent. *Tocher* found (by *Raoult's* method) the molecular weight of sesamin 311 (in benzene) and 312 (in acetic acid). *Villavecchia* and *Fabris*[3] obtained the molecular weight (by *Raoult's* method) 350 (in benzene), the formula $(C_{11}H_{12}O_3)_2$ demanding 384; *Bömer* and *Winter's* proposed formula $C_{33}H_{30}O_{10}$ leads to a molecular weight of 586.

3. A thick, non-crystallisable oil, free from nitrogen. This oil contains the substance which produces the characteristic reaction with sugar and hydrochloric acid (see below), a very minute quantity giving the crimson colour with these reagents (cp. *Tocher's* substance (*b*)). It should be noted that this chromogenetic substance entirely passes into the liquid fatty acids, if the latter be prepared by the lead-salt-ether method, in contradistinction to those olive oils (see below) which simulate sesamé oil in the *Baudouin* test (*Tortelli* and *Ruggeri*[4]).

The last-mentioned **colour reaction** is extremely characteristic of sesamé oil, so that it can thereby be detected with certainty in mixtures with other oils. This test, due to *Camoin*, generally, however, known as the *Baudouin* reaction, is the only colour reaction which has hitherto been found absolutely reliable in the analysis of oils and fats.[5] This colour reaction is all the more valuable as the chromogenetic substance is not destroyed by heating the oil to 250° C. for

[1] Merkling's (*Journ. Soc. Chem. Ind.* 1888, 45) statement that it is the glacial acetic acid extract which gives the characteristic colour reaction of sesamé oil requires therefore correcting.

[2] *Journ. Soc. Chem. Ind.* 1894, 69.

[3] *Annali del Lab. Chim. delle Gab.* iii. 1897, p. 22.

[4] *Chem. Zeit.* 1898, 601.

[5] With regard to the detection of sesamé oil in edible fats in the presence of "butter colours" by means of this reaction, see "Butterfat."

twenty minutes (*Tortelli* and *Ruggeri*). Nor can it be removed by filtering the oil over charcoal, as the author has ascertained by special experiment. *Baudouin's* test is usually carried out in the form recommended by *Villavecchia* and *Fabris.*

Baudouin's Test, as recommended by Villavecchia and Fabris.—Dissolve 0·1 grm. of sugar in 10 c.c. of hydrochloric acid of spec. grav. 1·19 in a test-tube, add 20 c.c. of the oil to be tested, shake thoroughly for one minute and allow to stand. The aqueous solution separates almost immediately. In the presence of even the smallest quantity of sesamé oil it will be found coloured crimson.

Villavecchia and *Fabris* attribute the chromatic reaction to the agency of levulose, or of substances produced by the action of hydrochloric acid on the latter; therefore glucose, maltose, and galactose cannot be used in place of saccharose. The main product of the interaction of levulose and hydrochloric acid being furfural, these chemists accordingly substitute the latter for the mixture of sugar and hydrochloric acid. Inasmuch as furfural itself gives a violet tint with hydrochloric acid, it is necessary to use a dilute solution; it has been found best to employ a 2 per cent alcoholic solution of furfural. The modified test is carried out in one of the following two forms:—

(*a*) Place 0·1 c.c. of the 2 per cent furfural solution in a test-tube, add 10 c.c. of the oil to be tested, and 10 c.c. of hydrochloric acid of spec. grav. 1·19; shake the mixture for half a minute and allow to settle. In the presence of sesamé oil, even if it be less than 1 per cent, the aqueous layer will acquire a distinct crimson colour. In the absence of sesamé oil the lower layer is either colourless, or has at most, as in the case of a very rancid though pure olive oil, a dirty yellow colour.

(*b*) Mix, as above, 0·1 c.c. of the alcoholic furfural solution with 10 c.c. of oil, and add 1 c.c. only of hydrochloric acid, agitate thoroughly and induce separation by addition of 10 c.c. of chloroform, when the aqueous layer will float on the top. Even less than 1 per cent of sesamé oil will be indicated by the crimson colouration of the aqueous layer.

These two methods have been tried with a large number of olive and arachis oils obtained from various localities, and further on rape (colza), cotton seed, linseed, walnut, poppy seed, neat's foot, blubber, and fish oils, and their complete reliability has been confirmed.[1] With regard to olive oils it should be noted that some Tunisian, Algerian, and Portuguese olive oils from Douro (*Domergue*, *Burker*, *Ferreira da Silva*), as also some Italian olive oils (*Lalande* and *Tambon*) from the province of Bari, Brindisi, and Lecce, give a colour reaction which may lead to doubt. In such cases *Milliau* relies on the colour test given by the fatty acids. Also *Tortelli* and *Ruggeri*[2] recommend to test the liquid fatty acids, since the chromogenetic substance of such abnormal olive oils does not

[1] Further confirmation is given by Wauters, *Journ. Soc. Chem. Ind.* 1896, 136.
[2] *Chem. Ztg.* 1898, 601.

pass into the liquid fatty acids. Thus, distinction between such olive oils, and olive oils adulterated with sesamé oils, is rendered feasible.

Hitherto the author has never met with a sample of sesamé oil that failed to give the *Baudouin* reactions, although his experience with sesamé oil extends over a large number of years and embraces a very large number of sesamé oils, both of edible and of commercial qualities.

It may, however, be pointed out that *Partheil*[1] failed to obtain the colour reaction with a sesamé oil extracted by means of chloroform from sesamé cake, and that *Weigmann*[2] and *Soltsien*[3] met with similar failure in the case of rancid sesamé oil. The same exceptional observation has been made by *Lauffs* and *Heismann*.[4] Curiously enough the last-mentioned chemists did obtain the *Baudouin* reaction on adding cotton seed oil; hence their statement requires revision.[5] *Soltsien's* test (colouration on treating with *Bettendorff's* reagent[6]) always fails if applied to rancid sesamé oil.

Considering the reliability of the *Baudouin* reaction, all "modifications," and other colour reactions that have been proposed, are of no importance. Therefore they are omitted in this treatise.[7]

Kreis[8] detected in sesamé oil a new substance, which he considers to be a phenol, as it combined with diazo compounds, hence he termed it "sesamol." According to *Malagnini* and *Armanne*[9] sesamol does not occur in the free state in sesamé oil, but as a complex body from which sesamol is set free on adding a mineral acid.

The drying power of sesamé oil is much less pronounced than that of cotton seed oil. In the *Livache* test, after seven days only 2·4 per cent of oxygen were absorbed; under the same conditions the fatty acids absorbed 2 per cent of oxygen after eight days.

In the elaïdin test sesamé oil becomes red after a short time, and acquires a dirty reddish-brown colour, yielding even after only twenty-four hours' standing a semi-fluid elaïdin.

The cold-drawn sesamé oil is largely used as an edible oil, notably so in the manufacture of margarine. Since small quantities of sesamé

[1] *Zeit. f. ang. Chem.* 1898, 730. [2] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1901, 131.
[3] *Ibid.* 1906, xii. [4] *Chem. Zeit.* 1907, 1023.
[5] Cp. Sprinkmeyer, *Zeit. f. Unters. Nahrgs. u. Genussm.* 1908, xv. 21. Kreis, *Chem. Zeit.* 1908, 87. Utz, *Chem. Revue*, 1908, 112.
[6] With regard to this test see Polenske, *Arb. a. d. Kais. Gesundheitsamt*, 1905, 570; Sprinkmeyer and Wagner, *Zeit. f. Unters. Nahrgs. u. Genussm.* 1905, x. 348; Feadler, *Chem. Revue*, 1905, 10; Soltsien, *Chem. Revue*, 1906, 138; Gerber, *Zeit. f. Unters. Nahrgs. u. Genussm.* 1907, xiii. 67.
[7] Cp. 2nd ed. of this work, pp. 391, 392. Bellier, *Ann. chim. analyt. applig.* 1899 217. Bömer, *Zeit. f. Unters. Nahrgs. u. Genussm.* 1899, 705. Breinl, *Chem. Ztg.* 1899, 647; Vandevelde, *Bull. de l'Ass. Belge*, 1900, May. Kreis, *Chem. Zeit.* 1902, 1014; 1903, 316, 1030. Tambon, *Journ. Pharm. et Chim.* 1901, 57. Utz, *Chem. Revue*, 1902 177; *Journ. Soc. Chem. Ind.* 1902, 1196.
[8] *Chem. Zeit.* 1903, 1030. [9] *Ibid.* 1907, 885.

oil are easily revealed by the *Baudouin* test, it has been made obligatory in Germany and Austria to use at least ten parts of sesamé oil in the manufacture of margarine for 100 parts of fatty matters (cp. "Margarine," Vol. III. Chap. XV.). In Belgium 5 per cent are prescribed. Sesamé oil is largely used in perfumery (for the extraction of balsam of Peru, sandalwood, etc.).

The best cold-drawn oil being rather high in price, adulteration of the best qualities with poppy seed oil, cotton seed oil, and arachis oil is not infrequent. The sesamé oils of second and third expression are adulterated with rape oil.

Poppy seed oil is detected by a higher iodine value than the normal one. For the detection of *cotton seed oil* the melting and solidifying points of the fatty acids should be determined. The iodine value of an *oil* suspected of being adulterated with cotton seed oil would not afford certainty. The iodine value of the liquid fatty acids, as also the determination of the tetrabromide, carried out under the conditions described in Vol. I. Chap. VIII., would furnish more reliable data. As confirmatory tests, the colour reactions of cotton seed oil described above should be resorted to.

Arachis oil is detected by the isolation of arachidic acid. The addition of arachis oil would lower the specific gravity of the sample.

The presence of *rape oil* would be ascertained by a low specific gravity of the sample, low solidifying and melting points of the fatty acids, and notably a low saponification value.

Sesamé oil is in its turn used as an adulterant of fatty oils, notably of poppy seed oil. Admixture of sesamé oil with other oils is, however, little practised, since the detection of the smallest quantity of sesamé oil is rendered easy by the *Baudouin* test.

The best oils are, as stated already, consumed as table oils; small quantities of this class are used in the production of perfumes ("enfleurage").

The lower qualities of sesamé oil find a large outlet for soap-making in the south of Europe; they are also used as burning oil and for making india-rubber substitutes.

BASSWOOD OIL[1]

French—*Huile de bois de tilleul.* German—*Lindenholzöl.*
Italian—*Olio di legno di tiglio.*

For table of characteristics see p. 180.

This oil is obtained from Basswood (*Tilia americana*, L.) by extracting rasped *wood* with ether. The tree is widely distributed in America from Virginia to the Alleghany Mountains, in Georgia, Nebraska, and Kansas.

[1] Weichmann, *Journ. Soc. Chem. Ind.* 1895, 665.

Physical and Chemical Characteristics of Basswood Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.
At 15° C. (Water 15° C. = 1).	° C.	Mgrms. KOH.	Per cent.
0·938	−10	178·1	111

The seeds from *Tilia parvifolia* (= *Tilia cordata*, Müll.) yield an oil, the characteristics of which will be described below in the table headed "Lesser known Semi-drying Oils."

LEMON PIPS OIL [1]

French—*Huile de pepins de citrons.* German—*Citronenkernöl.*
Italian—*Olio di semi del limone.*

On extracting dried and ground lemon pips with solvents, lemon pips oil is obtained as a pale yellow oil having a bland flavour recalling that of almond oil.

The sample examined by *Peters* and *Frerichs* had the acetyl value 13·65.

Physical and Chemical Characteristics of Lemon Pips Oil

Saponification Value.	Iodine Value.
Mgrms. KOH.	Per cent.
188·4	109·2

The fatty acids are stated to consist of palmitic, stearic, oleic, and linolic acids.

[1] W. Peters and G. Frerichs, *Arch. d. Pharm.* 1902 [240], 659 ; *Journ. Soc. Chem. Ind.* 1903, 102.

LUFFA SEED OIL, LOOFAH SEED OIL

French—*Huile de luffa.* German—*Schwammkürbiskernöl.*
Italian—*Olio di luffa.*

Physical and Chemical Characteristics of Luffa Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.
At 15·5° C. (water at 15·5 =1).	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refractometer. "Degrees."
0·9254	187·80	108·51	1·43	62·0 at 40° C.

This oil is expressed in East India from the seeds of *Luffa ægyptiaca*, Mill.; it is used by the natives as an edible oil. Small quantities of the seeds are exported from British Nigeria.[1]

The oil examined by *Crossley* and *Le Sueur*[2] was reddish brown in colour and had a slight odour.

The oil yielded 94·8 per cent insoluble fatty acids + unsaponifiable.

MYRTLE SEED OIL[3]

French—*Huile des sémences de myrte.* German—*Myrtensamenöl.*
Italian—*Olio di semi di mirto.*

The seeds of the common myrtle, *Myrtus communis*, L., contain 12-15 per cent of a fatty oil of distinctive taste and pleasant odour. The following characteristics have been ascertained :—

Specific gravity at 15° C.	0·9244
Saponification value	199·8
Iodine value	107·5
Reichert-Meissl value	9·65
Insoluble fatty acids + unsaponifiable	95·3 per cent.
Maumené test in Tortelli's thermoleometer	39° C.

The saponification value appears to me very low in view of the high *Reichert-Meissl* value. The number given for the *Maumené* test would also appear too low, considering the high iodine value, whereas olive oil (iodine value 83) gives in *Tortelli's* thermoleometer a rise in temperature of 44° C.

An examination of the fatty acids showed that the oil contains the glycerides of myristic, palmitic, oleic, and linolic acids. No stearic acid was found by *Hehner* and *Mitchell's* method.

[1] *British Nigeria*, by F. A. Mockler Ferryman, p. 318.
[2] *Journ. Soc. Chem. Ind.* 1898, 991.
[3] Scurti and Perciabosco, *Gazz. Chim. Ital.* 37 (1907), i. 483.

IKPAN SEED OIL [1]

French—*Huile d'ikpan.* German—*Ikpansamenöl.*
Italian—*Olio di semi di ikpan.*

This oil is obtained from the ikpan seed of Southern Nigeria; it is probably derived from a plant belonging to the *Curcurbitaceæ*. The seeds yield 40 per cent of a pale yellow oil from which, on standing, some "stearine" separates. The following characteristics have been ascertained :—

Specific gravity at 15° C.	0·9184
Saponification value	194·0
Iodine value	106·0
Insoluble fatty acids + unsaponifiable	95·9 per cent.
Titer test of fatty acids	36° C.

ANIS SEED OIL [2]

French—*Huile de graine d'anis.* German—*Anissamenöl.*
Italian—*Olio di semi d' anice.*

This oil is obtained from the seeds of *Pimpinella anisum*, L., after the ethereal oil has been driven off. The seeds contain over 25 per cent of a fatty oil, which has a slight odour resembling that of henbane seed oil. The fatty acids yield on oxidation tetra-hydroxy stearic acid (sativic acid). The oil absorbs 2·7 per cent oxygen in three days (determined by *Livache's* method). The specimen of oil examined by *Denjanow* and *Zypljankow* [2] had the acid value 6·3.

The following characteristics were determined :—

Oil—Specific gravity at 15° C.	0·924
Saponification value	178·3
Iodine value	105·3
Fatty acids—Solidifying point	0° C.
Iodine value	97·3 (?)

CROTON OIL

French—*Huile de croton.* German—*Crotonöl.*
Italian—*Olio di crotontiglio.*

tables of characteristics see p. 183.

The croton oil is obtained from the seeds of *Croton Tiglium*, L., a tree linolic acids of the *Euphorbiaceæ*, indigenous to the Malabar coast, and Southern Asia and China. The seeds contain 53-56 per

[1] W. Peters a... *Ind.* 1903, 102.

...*al Institute*, 1907, 132, 133.
...*ys. Chem. Ges.* 1905, 624.
... the occurrence of an enzyme in croton seeds, cp. Scurti and ... *Italiana*, 1907 (37), 486.

Physical and Chemical Characteristics of Croton Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	"Degrees."	Observer.
											26	1·4781	Harvey
15	0·9437	Dulière [3]	−7	Javillier	215	Lewkowitsch	106·6-109·1	Wijs	13·56	Lewkowitsch	Oleo-refractometer.		
15·5	0·9375 [1]-0·9428 [2]	Lewkowitsch			210·3	„	101·7-102 [6]	Lewkowitsch	13·27	„	°C.	"Degrees."	Observer.
100	0·8874	Dulière			215·6	Dulière	103·9-104·7	„	12·1	Dulière	22	+35	Dulière
					192·9 [4]	Javillier	109 [4]	Javillier			Butyro-refractometer.		
					194·5 [5]	„	108 [5]	„			°C.	"Degrees."	Observer.
											27	77·5	Dulière
											40	68	Lewkowitsch

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
88·9	Lewkowitsch	18·6-19 [7]	Lewkowitsch	201	Benedikt	111·2-111·8	Dulière
89·1	„						

[1] 53·4 per cent soluble in alcohol. [2] 24·4 per cent soluble in alcohol. [3] *Journ. Soc. Chem. Ind.* 1899, 1133 ; *Ann. Pharm.* 1899, 5, 229.
[4] Expressed oil ; acid value 27·3. [5] Oil extracted with ether ; acid value 30·9.
[6] A sample recently examined had the high iodine value of 122·3 (saponification value 210·2). [7] Titer test.

The oil has an amber-yellow, or orange, or brown colour according to its age, has a nauseous odour, a burning taste, and is a very powerful purgative. In pharmacy it is known as *Oleum crotonis.* According to *Kobert*[1] there are some kinds of croton oil in commerce that are miscible with *alcohol* in every proportion. This statement, however, only holds good of those oils that have been extracted from the seeds with alcohol. *Javillier*[2] states that oil obtained by expression or by extraction is only miscible with absolute alcohol if less than one volume be used; on mixing equal volumes of oil and absolute alcohol turbidity sets in, and with more alcohol complete separation into two layers is obtained, whereas oil extracted with alcohol is soluble in absolute alcohol in every proportion.

The author examined three specimens of croton oil prepared for pharmaceutical purposes by reliable firms. One volume of oil was shaken up with three and a half volumes of absolute alcohol. After separation into two layers had taken place, the amount of oil dissolved by the alcohol was determined quantitatively. The alcohol had dissolved from the three samples—24·4 per cent, 25·5 per cent, and 53·4 per cent respectively. The respective specific gravities of the oils were 0·9428, 0·9418, 0·9375. Hence croton oil can no longer be classed together with castor oil, and the comparative great solubility of the oil in absolute alcohol must be ascribed to the large proportion of glycerides of volatile fatty acids. The larger the proportion of free fatty acids the greater will be the solubility of the oil in absolute alcohol. Thus the above-mentioned specimen, of which 24·4 per cent dissolved in alcohol, contained 7·9 per cent free fatty acids.

Croton oil further differs from castor oil by its solubility in petroleum ether in all proportions.

The chemical composition of croton oil differs so widely from that of all other oils that its recognition by means of the quantitative reactions is easy. The author found 0·55 per cent of unsaponifiable matter in various specimens of croton oil. Croton oil is strongly dextro-rotatory (*Peter*[3]).

Croton oil is stated to contain the following fatty acids, partly as free acids and partly as glycerides: Stearic, palmitic, myristic, lauric, valeric (isobutyl formic), butyric, acetic, formic, oleic, linolic,[4] and tiglic. On standing, croton oil deposits some "stearine." "Croton-oleic acid," which was said to constitute the purgative principle of the oil, and was described as a non-volatile, unsaturated fatty acid, differing from oleic acid in that its barium salt was soluble in alcohol, is, according to *Dunstan* and *Bole*,[5] a resinous substance possessing a strong vesicating action.[6] Two samples

[1] *Chem. Zeit.* 1887, 416. [2] *Journ. Pharm. Chim.* [6], 7, 524.

[3] Cp. also Raknsin, *Chem. Zeit.* 1906, 143.

[4] Cp. Fokin, *Jour. Russ. Phys.-Chem. Soc.* 1907 (39), 607.

[5] *Journ. Soc. Chem. Ind.* 1895, 985.

[6] Its empirical formula is $C_{13}H_{18}O_4$; it is a hard, pale yellow, brittle resin, nearly insoluble in water, petroleum ether, and benzene, but easily soluble in alcohol, ether, and

examined by *Lewkowitsch*[1] had the true acetyl values 19·82 and 32·66 respectively.

Croton oil has weak drying powers; it thickens somewhat on exposure to air. It yields no solid product in the elaïdin test. Owing to the slight similarity between croton oil and castor oil, adulteration of croton oil with castor oil has occurred. Castor oil in croton oil would increase the specific gravity, lower the iodine value, and raise the acetyl value considerably.

ZACHUN OIL

French—*Huile de Zachun.* German—*Zachunöl.*
Italian—*Olio di Zachune.*

This oil is obtained from the seeds of *Balanites Ægyptiaca*, Delile, a tree found in northern tropical Africa, India, and Burmah.

The fruit, which is at first green, becomes red on ripening, and in its dry state somewhat resembles a date. The kernels contain 49·64 per cent (*Suzzi*[2]) or 41·2 per cent (*Milliau*[3]) of fatty matter. A specimen of seeds collected from Ghinda in Erythrea (Italian African colony) gave the following characteristics (*Suzzi*):—

Oil

Specific gravity at 15°	0·9200
Solidifying point	−0° to 5° C.
Saponification value	194·1
Iodine value	105·0
Maumené test	75·5° C.

Fatty Acids

Solidifying point	32-30·5° C.
Melting point	34·5-37° C.
Neutralisation number	200·0
Saponification value	201·6
Mean molecular weight	278·2

The samples contained 0·48 per cent free fatty acids (as oleic acid). The oil gave neither the *Halphen* nor the *Baudouin* reactions.

chloroform. On heating it softens gradually, and is quite fluid at 90° C. It has neither acid nor basic properties; it is decomposed by boiling with alkalis, yielding a mixture of acids, and loses thereby its vesicating properties. This seems to point to this substance being a lactone or an anhydride.

[1] *Analyst*, 1899, 319.

[2] *I semi oleosi e gli oli.* Published for the Milan Exhibition, 1906.

[3] *Agriculture pratique des pays chauds*, 1904, No. 16.

CURCAS OIL, PURGING NUT OIL, PHYSIC NUT OIL

French—*Huile de pignon d'Inde, de pulghère, de purghère, de médicinier.* German—*Curcasöl.* Italian—*Olio di curcas.*

For tables of characteristics see p. 187.

Curcas oil (*Oleum infernale*) is obtained from the seeds of *Jatropha Curcas*, L. (purging nut), by hot pressing. The plant is cultivated in tropical America and in all Portuguese colonies, chiefly in the Cape Verd Islands.[1] In Réunion the plant is cultivated as a support of the vanilla plant. (The bark of the plant is covered with a wax which consists of myricyl melissate (melissyl melissate), *J. Sack.*) The seeds consist of 66 per cent of kernels and 34 per cent of husks. The kernels yield on extraction with ether 52 per cent of oil, so that the oil contained in the whole seeds would amount to 34·3 per cent. The fresh oil has a pale colour, but becomes yellow with a reddish tint on exposure to the air. Its unpleasant odour is characteristic, and may serve to distinguish curcas oil from other oils ; it is further characterised by its strong purgative properties, which are much more pronounced than those of castor oil.

The acid values of commercial samples were found by *Lewkowitsch* and *Archbutt* 8·5 and 0·7 respectively. *Klein* obtained values varying from 0·57 to 4·96. The proportion of unsaponifiable matter—phytosterol—in the oil is 0·5 to 0·58 per cent (*Lewkowitsch* ; *Klein*). The acetyl value was found 8·4 (*Lewkowitsch*) and 9·8 (*Archbutt*). 100 parts of absolute alcohol dissolve at 15·5° C. about 2·17 volumes of oil (*Archbutt*). *Klein* found that alcohol (specific gravity not stated) dissolves 2·41 parts. The oil is insoluble in cold glacial acetic acid, but dissolves in the hot menstruum.

On standing at a temperature of about 12° C. a small quantity of solid glycerides separate. According to *Klein* curcas oil yields about 10 per cent of solid fatty acids (melting at 57·5° C., and solidifying at 53·5° C.) ; the liquid fatty acids consist of about equal proportions of oleic and linolic acids as ascertained by the relative quantities of their oxidation products, viz. dihydroxystearic and tetrahydroxystearic acids. The existence of isocetic acid (Vol. I. Chap. III.), stated by *Bouis* to occur in curcas oil, is doubtful.

The oil is used for soap-making, as an illuminant, and as a lubricating oil ; it can, however, hardly be considered suitable for the last-named purpose, as the oil dries in about 24 hours, cotton seed oil drying under the same conditions in 18-20 hours, and good rape oil in 48 hours (*Archbutt*).

The seeds of *Jatropha oligandra*, Müll., yield about 31·5 per cent of a fatty oil of the specific gravity at 14° C. 0·910, having purging properties.

The seeds of *Jatropha multifida*, L., yield 28·5 per cent of a fatty oil of the specific gravity 0·918 at 25° C.

[1] Klein, *Zeit. f. ang. Chem.* 1898, 1012.

Physical and Chemical Characteristics of Curcas Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At 25° C.	Observer.
15	0·9192	Horn	−8	Girard	−4	Lewko-witsch	193·2	Lewko-witsch	100·9	De Negri and Fabris	0·55	Lewko-witsch	65-66·6	Archbutt	1·4681-1·487	Klein
,,	0·920	De Negri and Fabris [1]	−8	Lewko-witsch									68·3	Suzzi [4]		
	0·915	Arnaudon and Ubaldini [2]							98·3	Lewko-witsch					Butyro-refractometer.	
	0·9199-0·921	Klein							104·9	Suzzi [4]						
15·5	0·9204	Lewko-witsch [3]													At °C.	"Degrees"
															25	65
															40	56·5

Observer.
Lewko-witsch
,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	Titer Test.	Observer.	°C.	Observer.	Per cent.	Observer.
95·5	Lewkowitsch	28·6	Lewkowitsch	24-26	De Negri and Fabris	105·05	De Negri and Fabris

[1] *Journ. Soc. Chem. Ind.* 1893, 453. [2] *Ibid.* 1893, 934. [3] *Chem. Revue*, 1898, 211. [4] Oil from Erythrean seeds.

BRAZIL NUT OIL

French—*Huile de noix de Brésil.* German—*Paranussöl.*
Italian—*Olio di noci del Brasile.*

For tables of characteristics see p. 189.

Brazil nut oil is obtained from the seeds of the Brazilian nut tree *Bertholletia excelsa*, Humb. and Bonp. The seeds bear the native name *kokobko.* They contain up to 73 per cent of the fatty oil, calculated to dry seeds,[1] the amount of water in the seeds being from 7-8 per cent.

The oil is of pale yellow colour and odourless; its taste is similar to that of the nuts themselves.

On standing, even at the ordinary temperature, the oil deposits "stearine." A sample examined by *Niederstadt*[2] contained 16 per cent of free fatty acids. In South America brazil nut oil is expressed for edible purposes. The nuts that have become mouldy in transit to Europe are expressed, and the oil thus recovered is used for soap-making, or as a substitute for inferior kinds of olive oil. An English patent (11,774, 1847, *J. B. Wilks*) claims the expression of Brazil nut oil for burning and lubricating purposes; the press cake to be used as cattle food and for manuring the land.

[1] Greshof, *Chem. Zeit.* 1906, 856.
[2] *Ber. d. deutsch. Pharm. Gesellsch.* 1902, 144.

[TABLE

Physical and Chemical Characteristics of Brazil Nut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9180	De Negri and Fabris	0·4	De Negri and Fabris	193·4	De Negri and Fabris	106·22 90·6	De Negri and Fabris[1] Niederstadt	50-52	De Negri and Fabris

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
31·1-32·25[2]	Lewkowitsch	28-30	De Negri and Fabris	108	De Negri and Fabris

[1] The iodine value of Brazil nut oil extracted with solvents is given by *De Negri* and *Fabris* as 93·8-95·1.
[2] Titer test.

MUCUNA OIL[1]

French—*Huile de mucuna.* German—*Mucunaöl.*
Italian—*Olio di mucuna.*

The seeds of the different species of Mucuna, viz. *M. urens*, *M. pruriens*, De C.,[2] *M. cylindro-sperma*, *M. monosperma*, contain this fatty oil.

The oil characterised in the following lines was obtained from *Mucuna capitata*, De C., a plant belonging to the *Leguminosæ* occurring in the Dutch Indies (described in Rumphius' *Herbarium Amboinensis* as *Cacara nigra*).

The oil was extracted with petroleum ether from the freshly ground seeds, the seeds yielding 2·08 per cent. The acid value of the oil was 6·7. The oil extracted from ground seeds which had stood for about two months showed a higher specific gravity, higher acid value, higher saponification value, and lower iodine value.

Amongst the solid fatty acids palmitic acid and stearic acid were identified. The acetyl value was determined by *Benedikt* and *Ulzer's* method, but in view of the strictures passed by the author on this method (Vol. I. Chap. VIII.), the number is not recorded here.

Physical and Chemical Characteristics of Mucuna Oil

Specific Gravity at 100° (water 15°=1)	Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per Cent.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ KOH.	Refractive Index. Butyro-refractometer. "Degrees" at 25° C.
0·865	3·5	16	178·22	103·95	0·77	66·2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Neutralisation Value.	Iodine Value.
195·6	112·9

SORGHUM OIL

French—*Huile de sorgho.* German—*Sorghumöl.*
Italian—*Olio di sorgo.*

This oil has been obtained from the dried seeds of *Sorghum cernuum*, Host., which is largely cultivated in Turkestan.

[1] W. P. H. Van der Driessen Mareeuw, *Pharm. Weekblad*, 1906, No. 9.

[2] This species appears to be identical with *Mucuna prurita*, Hook., the leaves of which are used for dyeing black.

The oil is characterised by a peculiar odour ; it represents a yellow vaseline-like mass ; it has, however, greater consistence.

Physical and Chemical Characteristics of Sorghum Oil

Specific Gravity at 15° C.	Melting Point. ° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9282	39-40	172·1	98·89	2·1

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Melting Point. ° C.	Iodine Value.
96·1	43-44	101·63
		Iodine Value of the Liquid Fatty Acids.
		148·08

This oil dries slowly ; the specimen examined by *Andrejew*[1] had an acetyl value of 6·85. The amount of lecithin calculated from the amount of phosphorus was 0·23 per cent. According to *Andrejew*, the mixed fatty acids of the oil consist chiefly of erucic acid, and small quantities of oleic, ricinoleic, and linolic acids. These statements stand in need of confirmation.

This oil must not be confounded with the oil from *Sorghum vulgare*.[2]

COUMOU OIL, PATAVA OIL[3]

French—*Huile de coumou.* German—*Comuöl.*
Italian—*Olio di coumou.*

For table of characteristics see p. 192.

Coumou oil is obtained from the kernels of the following two species of palm trees : *Œnocarpus patava*, Mart., and *Œ. bacaba*, Mart. The kernels are boiled out with water, when a pale yellow limpid oil —termed "patava oil"—rises.

[1] *Chem. Zeit.* 1903, Rep. 283. [2] *Chem. Rev.* 1904, 106.
[3] Bassière, *Jour. Pharm. Chim.* 1903, 323.

Physical and Chemical Characteristics of Coumou Oil

Saponification Value.	Iodine Value.	Reichert Value.
169·1 (?)	96·5	1·2

The oil is stated to be a semi-drying oil. The sample examined contained 4·3 per cent of free fatty acids. The extremely low saponification value cannot be reconciled with the statement made by *Bassière*, that the sample contained 95·7 per cent of insoluble acids + unsaponifiable, that it yielded 10·4 per cent of glycerin, and that the molecular weight of the fatty acids was 289·1. Nor can the statement that the sample contained 19 per cent of oleic acid be correct. The mixed fatty acids melt at 19° C.

PINOT OIL, PARA PALM OIL, PARA BUTTER [1]

French—*Huile de pinot*, *Beurre de Para*, *Beurre du palmier de Para*. German—*Pinotöl*, *Parapalmöl*, *Kohlpalmöl*, *Parabutter*. Italian—*Olio di pinot*.

Pinot oil is obtained from the kernels of *Euterpe oleracea*, Mart., known as the pinot or ouassey palm in Brazil and French Guiana. In the latter country it grows in profusion in the salt marshes of the lowlands, where it replaces the mangroves. These localities are known under the name "pinotières."

The oil is obtained by crushing the kernels and boiling them with water, when the oil rises to the top. In its fresh state pinot oil is a clear, slightly perfumed oil having a pleasant flavour.

Pinot oil is a semi-drying oil; on finely divided lead it absorbs 4·5 per cent of oxygen in four days. The fatty acids are stated to consist of 52 per cent of oleic acid and 48 per cent of solid acids. This statement is greatly at variance with the iodine value, given as 136. The saponification value also, stated to be 162·4, stands in need of confirmation. The mixed fatty acids are stated to melt at 12° C. The sample examined was six months old, and contained 42 per cent of free fatty acids. In Brazil and Guiana the fat is used in the fresh state for edible purposes.

Lesser known semi-drying oils, see table on opposite page.

[1] Bassière, *Jour. Pharm. Chim.* 1903, 323.

β. The Rape Oil Group

All the members of this group are obtained from seeds of plants belonging to the *Cruciferæ*.

Their drying powers are not of a marked character; the elaïdin obtained from them is a buttery mass.

Their most characteristic property is that they have much lower saponification values than any other vegetable oil, owing to the presence of erucin in these oils. Arachidic acid also appears to form a normal constituent, this acid having been found in a large number of rape oils, as also in a specimen of mustard oil.

The opinion held for a long time that these oils contain sulphur has been shown to be erroneous; all the "cold-drawn" rape oils are free from sulphur, and absence of that element in an oil does not, therefore, prove absence of rape oil. Presence of sulphur, however, may point to a rape oil which has been expressed at a high temperature or extracted with carbon bisulphide.

I describe under this group the following oils: Garden cress oil, ravison oil, hedge mustard oil, rape oil, black mustard oil, white mustard oil, radish seed oil, jamba oil.

GARDEN CRESS OIL

French—*Huile de cresson alénois.* German—*Gartenkressensamenöl.* Italian—*Olio di crescione.*

For tables of characteristics see p. 194.

Garden cress oil is obtained from the seeds of the garden cress, *Lepidium sativum*, L. The seeds contain from 23 to 25 per cent of oil.

The high iodine value of this oil, and especially its exceptionally high thermal reaction, place it nearer to the two oils from cruciferous plants described already, viz. cameline oil and garden rocket oil (drying oil), than to the other oils belonging to the rape oil group. Garden cress oil ranks, therefore, among the slowly drying oils.

In East India garden cress oil is used as an edible oil. Two specimens from Bengal and the Punjab, examined by *Crossley* and *Le Sueur*,[1] had the acid values 10·55 and 4·18 respectively.

On saponifying the oil, its peculiar odour disappears, and an unpleasant fish-like smell is noticeable, more strongly in the case of the extracted than the pressed oil. On liberating the fatty acids, the original odour again becomes noticeable, although it is not so strong as in the original oil.

[1] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Characteristics of Garden Cress Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.		Viscosity.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	Butyro-refractometer. "Degrees." At 40° C.	Observer.	Seconds at 70° F.	Observer.
15 (water at 15=1)	0·920	De Negri and Fabris	−6 to −15	Suzzi [1]	178	De Negri and Fabris	108-108·8	De Negri and Fabris	0·44-0·22	Crossley and Le Sueur	92-95	De Negri and Fabris			321·6	Crossley and Le Sueur
15·5 (water at 15·5=1)	0·9210-0·9221	Crossley and Le Sueur [2]			181·5-183·1	Crossley and Le Sueur [2]	101·72-118·4	Crossley and Le Sueur [2]			89·5	Suzzi [1]	60·5	Crossley and Le Sueur [2]		
20	0·9212 [3]	Wijs			186·4 [3]	Wijs	133·4 [3]	Wijs								
,,	0·9221 [4]	,,			185·6 [4]	,,	139·1 [4]	,,								
							128·5	Suzzi								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Iodine Value.		Neutralisation Value.		Mean Molecular Weight.	
Per cent.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer.
95·57	Crossley and Le Sueur	16-18	De Negri and Fabris	111·40	De Negri and Fabris	193·0 [3]	Wijs	291 [3]	Wijs
		20-21 [4]	Wijs	137·7 [3]	Wijs	193·4 [4]	,,	290 [4]	,,
				144·9 [4]	,,	186·7	Suzzi [1]		

[1] Oil from Erythrean seeds.

[2] Two oils from Bengal and the Punjab respectively.

[3] Expressed oil.

[4] Extracted oil.

RAVISON OIL

French—*Huile de ravison.* German—*Ravisonöl.*
Italian—*Olio di ravizzone.*

For tables of characteristics see p. 196.

The oil from Black Sea rape seed, a kind of wild *Brassica campestris* (cp. "Rape Oil," p. 198), is termed in commerce Black Sea rape oil or ravison oil. The seed contains 33-40 per cent of oil.

Ravison oil, like rape oil, contains small amounts of arachidic acid; thus 0·79 per cent of arachidic acid (of the melting point 70·4° C.) was found in a specimen.

The samples of ravison oil examined by *Archbutt* and *Deeley* [1] had acid values ranging from 4·8 to 12; the amounts of unsaponifiable matter varied from 1·45 to 1·66 per cent. In a genuine specimen examined in my laboratory even 1·83 per cent of unsaponifiable matter were found.

Ravison oil has a higher iodine value than rape oil and exhibits stronger drying properties. It is therefore not so suitable for lubricating purposes as the latter, and its admixture with (or substitution for) rape oil must be looked upon as adulteration. Since ravison oil is mostly extracted by means of solvents, traces of the latter are left in the oil. They are most readily detected by taking the flash point of the oil. A commercial oil examined by the author had the flash point 396° C. (in *Gray's* tester, Vol. III. Chapter XV.).

[1] *Lubricants and Lubrication*, p. 106.

[TABLE

Physical and Chemical Characteristics of Ravison Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.		Viscosity (Redwood's Viscosimeter).	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.		Observer.
15	0·9175-0·921	Cloëz	−8	Jean	174	Jean	105	Jean	45[1]	Jean	+25 +18[2] +16 to +20	Jean ,, Pearmain.	about 6-13% lower than refined Rape Oil 334-352 seconds at 70° F.	Archbutt and Deeley Lewkowitsch
,,	0·918-0·920	Itallie			177·9-179·3	Archbutt and Deeley	108·9-121·7	Archbutt and Deeley	65·8-76	Archbutt and Deeley				
15·5	0·9183-0·9217	Archbutt and Deeley					101·4	Tortelli and Ruggeri			Butyro-refractometer.		385 at 70° F.	,,
											At °C.	Degrees.	Observer.	95 at 140° F.	,,
,,	0·9146-0·9179	Lewkowitsch			172·9-177·2	Lewkowitsch	115·2-117·4	Lewkowitsch			20	74	Lewkowitsch	334 at 70° F.	,,
,,	0·9204	,,			178·5	,,	120·4	,,			25	71·5			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.			Iodine Value.	
°C.		Observer.	Per cent.	Observer.
100	0·8802	Archbutt and Deeley	126·1[3]	Archbutt and Deeley
			Iodine Value of Liquid Fatty Acids.	
			124·2	Tortelli and Ruggeri

[1] By Jean's thermelmameter. [2] Italian ravison. [3] Iodine value of the oil 121·7.

HEDGE MUSTARD OIL[1]

French—*Huile de ravenelle, huile de raphanistre.* German—*Hederichöl.* Italian—*Olio di rafano.*

Physical and Chemical Characteristics of Hedge Mustard Oil

Specific Gravity at 15° C.	Solidifying Point. ° C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9175	−8	174	105 (Hübl)

This oil is obtained from the seeds of the common hedge radish (runch, wild radish), *Raphanus Raphanistrum*, L. The seeds contain 35-40 per cent of oil, possessing a characteristic taste.

Hedge mustard oil closely resembles rape oil. It was expressed for the first time in 1880, with a view to substituting it for rape oil. It is detected in rape oil, according to *Valenta*, by treating 5 grms. of the sample with an amount of alcoholic potash which is insufficient for complete saponification, filtering the soap solution from the unsaponified oil, and adding strong hydrochloric acid to the filtrate, when a green colour is said to indicate the presence of hedge mustard oil.

RAPE OIL [COLZA OIL]

French—*Huile de colza.* German—*Rüböl.* Italian—*Olio de colza.*

For tables of characteristics see pp. 199-202.

The various kinds of rape oil are obtained from the seeds of *Brassica campestris* and of several largely cultivated varieties of this species belonging to the natural order *Cruciferæ.* The oils from these plants are, especially in this country, indiscriminately termed rape oil or colza oil; on the Continent, however, two different kinds of oil are understood under the last two names. According to the variety of the plant from which the seed is derived, the following oils may be broadly differentiated:—

1. Rape oil (French—*Huile de navette*; German—*Rapsöl, Repsöl*) from the seeds of *Brassica campestris*, var. *Napus*, L.

2. [Rubsen oil] French—*Huile de rabette*; German—*Rüböl, Rübsenöl*; from the seeds of *Brassica campestris*, var. *Rapa*, L.

[1] Valenta, *Dingl. Polyt. Journ.* 247, 36.

Both Brassica species furnish several, by no means sharply distinguished, varieties, which are again divided, according to the season of the year, into several forms. Thus *Brassica Napus oleifera biennis*, Roxb. (= *B. Napus B. oleifera*, D. C. = *B. N. oleifera hiemalis*, Doll.) yields the *winter variety* (Winterraps, Winterkohlraps, Setzölsamen, Lewat, Kohlraps, Kohlsaat or *Colza*); and the annual form, *Brassica Napus oleifera præcox*, Roxb. (= *B. N. annua*, Koch = *B. N. oleifera annua*, Metzg.), the summer variety (Sommerreps, Sommerkohlrepps, Sommerkohlsaat, Summercolza).

Brassica Rapa (= *B. asperifolia*, Lam. = *B. campestris*, L.) also is grown as a winter seed (*Br. Rapa oleifera*, D.C. = *B. R. oleifera biennis*, Metzg. = *B. campestris B. oleifera*, D. C. = *Br. R. oleifera hiemalis*, Martens) termed in Germany Winterrübsen, Winterölrübe, Wintersaat, Rübsaat; and, as a summer seed, *Brassica Rapa oleifera annua*, Metzg. (= *Br. campestris*, Koch = *Br. campestris*, L. = *Br. præcox*, Kitaibel = *Br. R. oleifera*).

Although the winter and summer varieties of rape oil differ in consistence, the summer oil being thinner and solidifying at a lower temperature, it is impossible to distinguish further the last-mentioned varieties by their chemical or physical characteristics. Moreover, as in the trade all three varieties are indiscriminately sold as *rape oil* or *colza oil*, I comprise within the two tables of the physical and chemical characteristics of the oil and its mixed fatty acids all the data that have been furnished by the several observers who have examined the rape oils of commerce. It is very desirable, however, that when characteristics of rape oil are published, full particulars as to variety and source be given. I therefore quote, by way of example, the following table :—

[TABLE

Characteristics of Genuine Rape Oils (Crossley and Le Sueur)

Name.	Variety.	Source.	Specific Gravity at 15·5° C. (water 15·5 = 1).	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable.	Refractive Index at 40° C.	Viscosity.		Acid Value.	Optical Activity in 200 mm. tube.
				Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refracto-meter. "Degrees."	Seconds at 70° F.	Compared with Water at 70° F.		
Brassica campestris	red	N.W. Provinces of India	0·9148	171·6	99·2	0·79	96·3	...	390·6	15·38	2·90	− 7
,, ,,	glauca	,,	0·9142	171·4	97·7	0·67	95·04	59·2	402·6	15·85	1·78	− 10′
,, ,,	dichotoma	,,	0·9154	172·2	104·8	0·22	95·57	...	371·8	14·64	1·57	...
,, ,,	...	Punjab	0·9163	173·4	96·25	0·43	94·56	...	393·2	15·48	2·57	...
,, ,,	brown	Bombay	0·9171	172·8	94·1	0·00	...	...	464·6	18·29	4·00	...
,, ,,	yellow	,,	0·9141	169·4	96·66	0·00	...	...	413·8	16·29	1·42	− 5′
,, napus	...	Bengal	0·9146	167·7	97·7	0·00	95·55	58·8	398·0	15·67	3·77	− 15′
Eruca sativa	allied to mustard	Bombay	0·9177	170·4	99·72	0·66	95·49	...	371·0	14·61	2·10	...
,, ,,	,, ,	Punjab	0·9152	169·0	97·41	0·11	...	...	405·8	15·98	3·70	− 11′
,, ,,	,, ,,	Cawnpore	0·9165	174·1	99·10	0·77	...	...	369·4	14·54	2·51	− 18′

Physical and Chemical Characteristics of Rape Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·914-0·917	Allen	−4 to −6	Girard	178·7	Köttstorfer	100·8-102·4	Archbutt	0·25	Reichert
,,	0·9142	Souchère [1]	0	Holde	177	Valenta	97·8 [4]	,,	0·3-0·4	Meicus
,,	0·9151	,, [2]	−10	Lewko-	175-179	Allen	99·1-105·6 [7]	Thomson and		and
,,	0·9150-0·917	De Negri and	(Summer	witsch	170-176·4	Archbutt [3]		Ballantyne		Scherer
		Fabris [1]	variety)						0·0-0·79	Crossley and
15·5	0·9133-0·9168 [7]	Thomson and	+10	,,	175 [4]	,,	97·65-102·1	De Negri and		Le Sueur [2]
		Ballantyne	(Winter					Fabris		
,,	0·9132-0·9159	Archbutt [3]	variety)		170·6-175·3	Thomson and	94·1-104·8	Crossley and		
						Ballantyne		Le Sueur [5]		
15·5 (water	0·9141-0·9177	Crossley and			175-177	De Negri and	98-103·6	Lewkowitsch [6]		
15·5 = 1)		Le Sueur [5]				Fabris	93·5	Lewkowitsch		
23	0·910	Dieterich			177-178	Oliveri				
99	0·8632	Allen			171·7-176·5	Lewkowitsch [6]				
(water 15·5 = 1)					167·7-173·4	Crossley and Le Sueur [5]				

[1] Colza oil. [2] Rape oil. [3] Fifty-two samples. *Journ. Soc. Chem. Ind.* 1886, 310.
[4] From Guzerat seed. [5] Indian oils ; cp. p. 199. [6] Commercial rape oils of good quality.
[7] It should be noted that the sample giving the highest value 105·6 had the highest specific gravity 0·9168, and it is therefore open to doubt whether that sample represented genuine rape oil from cultivated seed.

Physical and Chemical Characteristics of Rape Oil—continued

Thermal Tests.				Refractive Index.			Viscosity (Redwood's Viscosimeter).	
Maumené Test.		Heat of Bromination.						
°C.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
55-64	Archbutt	18·4	Hehner and	15	1·4720-1·4757	Strohmer	370-380	Lewkowitsch
51-60	Allen	17·6	Mitchell	20	1·4735	Holde	369·4-	Crossley and
49-51	De Negri and Fabris	17·3	Jenkins	20	1·4726-1·4742	Harvey	464·6	Le Sueur
		17-20·3	Archbutt	60	1·4667	Thoerner		
Specific Temperature Reaction.				Oleo-refractometer.				
				"Degrees" at 22° C.		Observer.		
125-144	Thomson and Ballantyne			+15 to +18·5		Jean		
				+16 to +20		Pearmain		
				Butyro-refractometer.				
				At °C.	"Degrees."	Observer.		
				25	68	Mansfeld		
				40	58·8-59·2	Crossley and Le Sueur [1]		

[1] Indian oils. Cp. p. 199.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·1	Bensemann	99 (water 15·5 = 1)	0·8438	Allen	18·5	Allen	18·3-19·5	Allen	185	Thoerner	321·2	Allen	96·3-99·02	Morawski and Demski	1·4991	Thoerner
94·56-96·3	Crossley and Le Sueur [1]	100 (water 100 = 1)	0·8758	Archbutt	18-17	Bensemann [4]	21-22	Bensemann [5]			307 (?)	Williams	105·6	Williams		
							18·5-21	Archbutt			314	Valenta	99·8-103·1	De Negri and Fabris		
							16-19	De Negri and Fabris					103·6 [6]	Wijs		
					16	Thoerner	20	Thoerner					Iodine Value of the Liquid Fatty Acids.			
					Titer Test.								120·7	Wallenstein and Finck		
					12·7-13·6 [2]	Lewkowitsch							124·2-125·5 [7]	Tortelli and Ruggeri		
					11·7-12·2 [3]	,,							114·3 [8]			

[1] Indian oils; cp. p. 199. [2] Colza oil. [3] Rape oil. [4] Point of incipient fusion. [5] Point of complete fusion.
[6] Cold pressed. [7] Iodine value 102·2-101·7. [8] Very old sample, iodine value = 96·4.

For further numbers cp. p. 208.

Rape seed is grown in almost all European countries. In France and in Belgium the winter variety of *Brassica Napus* is chiefly grown. Enormous quantities are grown in East India, and the bulk of the East Indian seed is imported into England from Calcutta, Madras, Bombay, Guzerat,[1] and Ferozepore. The following tables give the amounts of rape seed worked up by the United Kingdom, France, and Germany :—

Rape Seed imported into the United Kingdom

Countries.	1902.	1903.	1904.	1905.	1906.	1907.
	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.
Russia	28,264	104,980	154,263	35,690	10,985	25,058
Germany	4,956	4,145	4,130	3,265	1,953	2,819
Holland	4,287	2,972	2,237	2,769	3,263	4,100
Belgium	1,893	107	602	4,453	3,411	982
France	967	330	321	1,001	757	1,512
Roumania . . .	16,414	47,907	46,467	41,960	9,202	3,432
Argentine Republic . .	640	26	245	270	738	...
Other foreign countries .	1,827	...	1,173	...	...	...
Bombay	78,567	75,995	49,999	72,306	68,758	203,765
Bengal	80,382	4,477	30,541	13,998	19,082	9,535
Madras	8,560	67,357	19,333	5,614	...	8,995
Other British possessions .	1,521	...	...	...	...	1,762
Total[2] . .	228,278	308,296	309,325	181,326	118,149	261,960

Rape Seed Production in France and Imports into France

(Double hundredweights)

Year.	Production.		Imports.		
	Colza.	Navette.	European Colza.	Navette.	Indian Rape Seed including Mustard Seed.
1896	...	...	64,017	27,898	460,936
1897	572,993	55,635	55,652	114,457	539,131
1898	638,236	53,507	19,244	43,164	258,104
1899	620,163	51,778	11,470	19,653	647,271
1900	425,310	35,165	150,164	452,252	299,890
1901	379,332	30,349	48,420	223,175	579,293
1902	388,943	36,489	116,095	334,452	605,226
1903	376,435	37,161	47,927	21,298	780,664
1904	527,541	54,361	22,449	2,539	580,071
1905	...	...	69,246	300,948	209,093
1906	...	...	8,126	19,080	495,687
1907	...	...	1,379	2,174	605,397

[1] The species yielding the Guzerat seed is known as *Brassica glauca*.

[2] The totals are the quantities actually imported ; they do not represent in every case the sum of the specified items.

Rape Seed imported by Germany

(Double hundredweights)

Year.	From			
	India.	Russia.	Other Countries.	Total.
1896	35,178	42,770	12,334	90,282
1897	78,946	23,183	17,966	120,095
1898	94,752	16,566	8,973	120,291
1899	76,909	21,462	6,950	105,321
1900	62,373	22,170	47,371	131,914
1901	119,290	14,630	31,520	165,440
1902	102,480	13,650	34,460	150,590
1903	74,260	22,870	16,930	114,060
1904	117,780	8,910	6,510	133,200
1905	69,890	19,530	71,540	160,960
1906	53,258	7,410	24,928	85,596
1907	140,873	7,996	7,868	156,737

Rape seed is crushed between rollers, and the meal is either expressed or extracted with carbon bisulphide or petroleum ether. The extracted oil is, as a rule, purer than the expressed oil, since a considerable amount of mucilaginous matter passes into the oil when the seed is expressed. The cakes obtained by expression form an excellent cattle food if the seed has been tolerably pure, *i.e.* free from mustard seed and wild seeds. The extracted meal is unsuitable as cattle food, and is chiefly used as manure, at any rate in this country, although some meal, especially on the Continent, finds its way into compound cakes.

Rape (colza) seed contains from 33 to 43 per cent of oil. The seed harvested in the North of France contains 43 to 45 per cent; Danubian seed 38 to 40, and Indian seed from 42 to 45 per cent.

The crude oil is dark in colour, and before being put on the market it is refined by treatment at the ordinary temperature with about one per cent of strong sulphuric acid (*Thénard's* process), which coagulates and carries down the impurities. The settled oil is then washed with water until free from mineral acid. The black waste acid does not seem to be recovered. *Goffart*[1] proposed to convert it into a consistent grease by heating with zinc.

The refined oil of commerce is pale yellow; it possesses a characteristic smell [which may serve to identify the oil] and, except for the finest qualities, an unpleasant harsh taste. The term "colza oil" can no longer be taken as referring to the special oil, expressed from the finest French seed, as was the case about forty years ago. For as the consumption of colza oil extended, the seeds from other countries were used for the manufacture of "colza oil," especially German seed, such as rubsen seed from *Brassica campestris*, var. *rapa*. Since Indian

[1] French patent 350,001.

rape seed is being refined in large quantities, the term "colza oil" has become a generic term, denoting a refined rape oil from the various kinds of rape seed. Therefore, the restriction of "colza oil" to a French oil or even a German oil no longer holds good, and "colza" oils are sold in trade which are made from Indian seed, such as Cawnpore seed and Guzerat seed. It should be noted that "colza oil" was originally an oil which had been obtained by expression, and the term "best refined colza oil" must still be held as rightly belonging to an expressed oil such as is used for edible purposes. This class of edible rape oil is largely used by bakers for greasing the ends of loaves in the oven ("bread oil"). *Linde*[1] heats rape oil with bread crumbs or milk to about 180° C. so as to impart to it a peculiar taste.

There are also in the trade pure refined colza oils which have been obtained by extraction with solvents. These are of distinctly inferior quality, and their taste reveals their origin immediately. Colza oils of this class are not objectionable as burning oils, but being, as stated already, of a distinctly inferior quality, they are valued in commerce at a lower figure.

Jamba oils (see p. 221) approximate rape oils as regards quality; as these jamba oils are now coming in larger quantities on the market the distinction between rape oils and jamba oils has gained some importance (see p. 221).

Glycerides of the saturated fatty acids occur in rape oil to a small amount only. *Tolman* and *Munson* found by the lead-salt-ether method 1·02 per cent (and less) of solid fatty acids. What *Reimer* and *Will*[2] termed behenic acid in rape oil has been shown by *J. E. Alén*[3] and *Ponzio*[4] to be in reality crude arachidic acid (*i.e.* a mixture of arachidic acid and lignoceric acid). *Archbutt*[5] confirmed the occurrence of "arachidic acid" in a number of commercial rape oils. His observations are reproduced in the following table :—

Origin of Oil.	Crude Arachidic Acid.	
	Per cent.	Melting Point. °C.
Crude, several years old, from Rubsen	0·59	69·2
Crude, several years old, from Raps	0·36	69·0
Kustendje (Black Sea)	0·84	70·4
Refined, Stettin	1·14	69·0
	After purification by one recrystallisation from 90 per cent alcohol,	
	0·91	72·2
Oil prepared in the Laboratory from Guzerat seed	1·61	71·1
	After purification by twice recrystallising from 50 c.c. of 90 per cent alcohol,	
	1·43	73·1

[1] United States patent, 692,187. [2] *Berichte*, 1887, 2388.
[3] *Svensk Kemisk Tidskrift*, 1892, 78; 1893, 179.
[4] *Journ. f. prakt. Chemie*, 1893 [48], 487; *Journ. Soc. Chem. Ind.* 1894, 257.
[5] *Journ. Soc. Chem. Ind.* 1898, 1009.

Amongst the unsaturated fatty acids, erucic and rapic acids have been identified. Since the iodine value of the unsaturated liquid fatty acids lies in the neighbourhood of 120, whereas the respective iodine values of rapic and erucic acids are 90·07 and 85·81, the presence of unsaturated fatty acids belonging to the linolic, or to the linolenic series must be suspected. Indeed *Hehner* and *Mitchell* obtained 3·6 per cent of a brominated acid melting at 179° C.; the same compound was also isolated by *Farnsteiner*, and by *Walker* and *Warburton* in the author's laboratory; the last-named observers obtained 2·4 to 3·4 per cent of ether-insoluble bromide.

On standing, "stearine" separates from rape oil at the ordinary temperature. *Halenke* and *Möslinger*[1] examined a species of rape "stearine" with the following result :—

	Melting Point. °C.	Saponification Value.
Fat	38·5	161·76
Fatty acids . .	34	160·05

It follows from these numbers that the "stearine" consisted almost entirely of trierucin.

Reimer and *Will*[2] obtained from a specimen of crude rape oil "stearine," by dissolving the solid mass in ether, filtering and precipitating with alcohol, colourless needles having the melting point 47° C. They were pure dierucin. The formation of dierucin is due to hydrolysis of the oil having been arrested at the first stage[3] (see Vol. I. Chap. II.).

According to *Norman*,[4] dierucin, which is frequently met with in crude oil, has never yet been found in refined oil.

The unsaponifiable matter contained in rape oil varies from 0·5 to 1 per cent. This figure is rarely exceeded. Rape oils containing larger amounts of unsaponifiable matter, exceeding say 2 per cent, should be looked upon with suspicion. *Windaus* and *Hauth*[5] state that the phytosterol from rape oil consists of a mixture of the ordinary phytosterol and stigmasterol (Vol. I. Chap. I.).

It appears that *Siegfeld*[6] had the stigmasterol acetate in his hands, for after having prepared the rape oil phytosteryl acetate, melting after the fifth crystallisation at 135·5° C.-136·5° C., he found in the mother liquors an acetate which melted after the thirteenth crystallisation at 145·6° C.-146·6° C.

Commercial rape oil as a rule contains free fatty acids. In view of the importance which the proportion of free fatty acids has on the

[1] *Corresp. d. Vereins d. bayer. Chem.* No. 1.
[2] *Berichte*, 1886, 3320. [3] Cp. C. L. Reimer, *Berichte*, 1907, 256.
[4] *Chem. Zeit.* 1907, 211. [5] *Berichte*, 1906, 4378.
[6] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1904, vii. 581.

valuation of commercial rape oils intended for lubricating purposes and for burning, I collate in the following table some numbers found by various observers :—

Free Fatty Acids in Rape Oils

Description of Oil.	No. of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
		Per cent.	
...	1	4·28	Salkowski
...	1	6·64	Rechenberg
Sweet oil	3	0·53–1·82	Nördlinger
Commercial oil, expressed .	9	0·52–6·26	,,
,, ,, extracted .	2	0·77–1·1	,,
,, ,, . . .	5	2·43–6·24	Thomson and Ballantyne
,, ,, . . .	50	1·7–5·5	Archbutt
,, ,, . . .	5	1·05–3·9	Deering
Indian oils . . .	10	0·7–2·01	Crossley and Le Sueur

In *Livache's* test rape oil absorbs 2·9 per cent of oxygen after seven days, whereas the fatty acids absorb only 0·9 per cent after eight days. The oil thickens and becomes rancid without, however, drying. Rape oil may, therefore, be considered as representing a class of oils occupying an intermediate position between the semi-drying and the non-drying oils.

It is most likely due to this slight drying power that old rape oil samples exhibit notable acetyl numbers. Thus *Lewkowitsch* found in a sample of old colza oil the acetyl value 14·7, and *Gripper* values varying from 24 to 41·7.

The following table, due to *Gripper*,[1] gives the characteristics of a number of old rape oils which had been standing in corked bottles in full daylight for the times stated. For comparison, the numbers obtained for fresh rape oil are added. It appears that air must have had access to the oil, as the specific gravities and viscosities, as also the acetyl numbers and soluble fatty acids, had increased, whilst the iodine values had decreased.

[1] *Journ. Soc. Chem. Ind.* 1899, 342.

[TABLE

	Specific Gravity at 60° F.	Free Fatty Acids as Oleic Acid. Per cent.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable.	Soluble Fatty Acids, equivalent to per cent KOH.	Viscosity at 60° F. Rape Oil at 60° F. =100.	Insoluble Fatty Acids.			
									Melting Point. °C.[1]	Molecular Weight.	Iodine Value.	Acetyl Value.
Rape oil, 8 years 9 months old	0·9356	13·35	197·2	63·89	20·2	89·1	3·48	1163	21·1	326·1	72·07	41·73
,, ,, 6 ,, 6 ,, ,,	0·9478	8·19	195·7	70·83	...	90·34	...	750 (about)	16·7	320·0	...	...
,, ,, 7 ,, 5 ,, ,,	0·9441	7·98	194·3	72·06	15·7	90·17	2·80	587	18·1	320·0	79·06	38·78
,, ,, 7 ,, 10 ,, ,,	0·9414	11·04	188·4	71·52	...	89·91	2·47	515	17·2	320·0	77·28	35·39
,, ,, 9 ,, 1 ,, ,,	0·9265	6·76	180·9	83·37	...	92·90	1·63	214	20·0	324·6	86·02	28·72
,, ,, 10 ,, 1 ,, ,,	0·9287	8·38	180·6	90·38	...	92·67	1·51	245	18·3	314·4	...	...
,, ,, 4 ,, 8 ,, ,,	0·9196	4·22	179·4	94·35	...	94·34	1·12	145	18·1	320·5	98·23	...
,, ,, 8 ,, 2 ,, ,,	0·9197	5·62	181·7	98·90	...	94·07	0·95	131	16·1	320·5	103·93	25·71
,, ,, 9 ,, 8 ,, ,,	0·9156	4·82	176·7	98·64	...	95·04	0·67	115	17·8	329·0	...	...
,, ,, 4 ,, 0 ,, ,,	0·9142	4·30	178·0	96·92	4·2	95·70	0·67	110	18·3	320·5	...	...
,, ,, 6 ,, 0 ,, ,,	0·9170	5·74	180·4	101·34	...	96·00	0·78	104	17·2	324·6	107·12	28·94
,, ,, 5 ,, 2 ,, ,,	0·9167	4·32	178·6	100·35	...	95·70	0·69	102	19·1	320·5	104·17	24·45
Rape oil, fresh . . .	0·9140	2·70	177·8	99·08	...	95·60	0·39	100	20	...	...	23·11

[1] Determined by the Crossley and Le Sueur method.

The changes which rape oil undergoes on blowing with air at 100° C. have been investigated by *Procter* and *Holmes*.[1] Their results are reproduced in the following table :—

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0	0·911	1·4748	120·0
3	0·913	1·4749	97·0
6	0·913	1·4750	94·0
9	0·913	1·4750	90·0
12	0·913	1·4751	89·0
15	0·914	1·4754	89·0
18	0·915	1·4756	88·0
21	0·919	1·4756	87·0
24	0·922	1·4758	86·0

The **elaïdin test** does not give characteristic indications.

Rape oil is largely adulterated with the following fatty oils: linseed, hemp seed, poppy seed, cameline, cotton seed, ravison, and hedge mustard oils, and refined fish and blubber oils. Paraffin and rosin oils are also frequently added fraudulently.

In order to "correct" the specific gravity, which may have been raised by the addition of the last-named two oils, sperm oil is also added. The unsaponifiable paraffin and rosin oils are easily detected by estimating the amount of *unsaponifiable matter*. The presence of sperm oil also increases the amount of unsaponifiable matter, since it contains 37 to 41 per cent of unsaponifiable substances. Hence, the examination of the unsaponifiable matter for the presence of sperm oil alcohols may become necessary in special cases. (Cp. Chap. IX.)

The addition of large quantities of linseed, hemp seed, poppy seed, cameline, fish and blubber oils will be readily recognised by the iodine value, and chiefly by the determination of one of the following characteristics: specific gravity, melting point of the fatty acids, thermal tests, saponification value, and also the viscosity of the oil.

The **specific gravity** of rape oil rarely exceeds 0·916, and this may be considered for practical purposes as the limit, although, as will be seen from the table given above, higher values have been recorded.[2] Of fifty-two samples examined by *Archbutt*—

7 samples had a specific gravity below 0·9140
27 ,, ,, ,, above 0·9139 but below 0·9150
18 ,, ,, ,, ,, 0·9149 ,, 0·9160

The specific gravities of the other fatty oils that may be used as adulterants being higher than 0·9160, a sample of oil the specific gravity of which exceeds that figure must be looked upon with

[1] *Journ. Soc. Chem. Ind.* 1905, 1287. [2] Especially in the case of Japanese oils.

suspicion. Of course, presence of an unsaponifiable oil cannot be detected by determination of the specific gravity alone; it has been pointed out already that the specific gravity of an adulterated oil is usually "corrected."

The **melting point of the fatty acids** and the **solidifying point** (titer test), will be higher than the normal one if cotton seed oil has been added; on the other hand, it will be lowered by the presence of linseed oil or of any of the other oils mentioned above. If cotton seed oil be suspected, the *Halphen* colour reaction may be used as a confirmatory test. In case heated cotton seed oil had been used, this test will fail. The nitric acid colour test is too uncertain in the presence of rape oil to be relied upon.

The **thermal test** with sulphuric acid or bromine[1] is still largely used, although the indications furnished by the iodine value are much more reliable. The thermal reactions will indicate admixture of linseed or other drying oils, or semi-drying oils, such as cotton seed oil.

The **saponification value** of the sample under examination will easily lead to a decision as to whether any other fatty oil, with *the exception of an oil belonging to the rape oil group, such as ravison or hedge mustard oil*, is present. In consequence of the large proportion of erucin in rape oil, its saponification value is very low, lower than that of any of the fatty oils mentioned above. [Castor oil, which is also characterised by a low saponification value, would be detected by the specific gravity and acetyl value.] It should, however, not be forgotten that a low saponification value will also be found if unsaponifiable oils are present, in which case the latter must be separated first, and the neutralisation value of the fatty acids determined subsequently.

The following are the saponification values of the fifty-two samples of rape oil examined by *Archbutt*:—

4	samples	170	to	171
12	,,	171	,,	172
9	,,	172	,,	173
14	,,	173	,,	174
11	,,	174	,,	175
1	,,	175	,,	176
1	,,	176	,,	177

It may be repeated that the other members of the rape oil class also have low saponification values.

The determination of the **iodine value** should not be omitted, for this number affords valuable guidance as to the presence of oils which belong to the rape oil group but are not derived from the cultivated seed. Such oils (ravison oil, etc.) cannot be detected by the saponification value alone, but they reveal their presence by somewhat high iodine values, especially if the latter be associated with high specific gravity numbers. The figures given in the table of "characteristics"

[1] Cp. Archbutt, *Journ. Soc. Chem. Ind.* 1897, 311.

under the heading "iodine value," as also the numbers given in the following table, will furnish further information :—

Characteristics of Genuine Rape Oils and Allied Oils (Lewkowitsch)

	Specific Gravity at 60° F. (water at 60°=1)	Saponification Value.	Iodine Value.	Viscosity.		Unsaponifiable Matter. Per cent.
				At 70° F.	At 140° F.	
Genuine rape oil, crude	0·91458	173·1	106·8			
,, ,, refined	0·91364	173·1	104·4	380		
,, ,, ,,	0·9139	172·9	102·1			
,, ,, ,,	0·9145	173·2	103·6	375	...	3·13
,, ,, ,,	0·9146	172	103·5	...	94	
,, ,, ,,	0·9147	173	104·6	...	92	1·43
,, ,, ,,	0·9147	172·5	103·1	...	94	1·56
,, ,, ,,	0·9153	176·6	102·9	...	91	1·42
German "colza" oil containing mustard seed oil	0·9161	175·3	106·5			
Rape oil, second quality	0·91629	175·8	110·3	360		
Ravison oil[1]	0·91793	177·4	114·7	329		
,, ,,	0·9204	178·5	120·4	334	...	2·29

It may be added that the iodine numbers 98-103·6 given by the author in the table of "characteristics" have been derived from special investigations of a very large number of genuine rape oils (from cultivated seed). The number 93·5 given in that table is exceptionally low.

The determination of the **viscosity** of rape oil is a very valuable means of ascertaining its purity. It will be found best to compare the sample with a standard rape oil of known purity, as the viscosity of rape oil is fairly constant. Since no other oil likely to be used as an adulterant, with the exception of castor oil, possesses so high a viscosity as rape oil, the genuineness of the sample can thus be ascertained.

The **Valenta test** is very characteristic of rape oil, and will prove useful as an additional means of deciding whether a sample is genuine or not.

Fish oils and **blubber oils** in rape oil may be recognised by their peculiar smell and taste, especially on warming, and also by the intensity of the phospho-molybdic acid reaction. More important evidence will be furnished by the determination and examination of the ether-insoluble bromide prepared from the mixed fatty acids. Unmistakable evidence will be furnished by the phytosteryl acetate test (cp. "Linseed Oil," p. 59), as also by the iodine value of the oil and of its liquid fatty acids.

Since rape oil is refined with concentrated sulphuric acid, commercial oils should be tested for the presence of sulphuric

[1] Cp. also "Ravison Oil," p. 196.

acid by shaking the oil with warm water and examining the aqueous layer.

The detection of rape oil in *other oils* by means of colour reactions (such as *Mailho's* or *Schneider's* reagents), purporting to show presence of sulphur, can no longer be considered as useful, since it has been proved that sulphur is not a constitutive element of the oils obtained from the seeds of *Cruciferæ*. The "cold-drawn" oils of commerce are completely devoid of sulphur, but oils extracted by means of carbon bisulphide may retain some sulphur, it being difficult to remove the last traces of the solvent. The colour reaction proposed by *Palas*[1] for the detection of rape oil in olive oil (viz. agitation with rosaniline sulphite) is valueless, as experiments instituted by the author have shown.

Rape oil in other oils will be detected by its characteristic smell and taste, and by the influence it exercises on the characteristics of the oil under examination, such as the iodine value of the oil, the iodine value of the liquid fatty acids, and chiefly on the saponification value.

The "cold-drawn" oil is used as an edible oil, especially in India. It is also used as an edible oil on the Continent, and in this country as "bread oil" (see p. 205). The various qualities of refined oil have been mentioned above. Those colza oils which are unsuitable for edible purposes find an outlet as excellent burning oils. Equally well-refined oils can also be used as wool oils. Enormous quantities of the oil are used for lubricating purposes, both in the refined state and as "blown rape" oil (see Vol. III. Chap. XV.). Smaller quantities are used on the Continent for the making of soft soap.

Charlock oil, from the seeds of *Sinapis arvensis*, wild mustard charlock, frequently contaminates rape oil.

The oil itself is not a commercial article, since the endeavour of the rape seed growers is directed to the destruction of the charlock plant as being a weed.

BLACK MUSTARD SEED OIL

French—*Huile de moutarde noire.* German—*Schwarzsenföl.*
Italian—*Olio di mostarda nera.*

For tables of characteristics see pp. 214, 215.

Black mustard seed oil is obtained from the seeds of *Sinapis nigra*, L. (*Brassica nigra*), which contain 31-33 per cent of oil. The oil has a brownish-yellow colour, and possesses a mild taste; it smells of ethereal mustard oil.

In its chemical composition it closely resembles rape oil. *Tolman* and *Munson* obtained from various samples by the lead-salt-ether

[1] *Journ. Soc. Chem. Ind.* 1897, 361.

method from 2·32-4·05 per cent of solid fatty acids. Amongst these occurs arachidic acid; amongst the unsaturated acids erucic and a liquid fatty acid [1] (rapic acid ?) have been found.

Nördlinger found in two samples of the oil free fatty acids to the extent of 0·68 and 1·02 per cent, calculated to oleic acid.

The oil is obtained as a by-product in the manufacture of ethereal mustard oil. It is not suitable for burning; it is, therefore, used for soap-making. Efforts have been made lately to introduce this oil, under the name "Sinapol," for cosmetic and pharmaceutical purposes, as a substitute for olive oil.

The oil from Indian mustard seed, *Brassica* (*Sinapis*) *juncea*, D. C. (a variety of *Sinapis nigra*), has been examined by *Crossley* and *Le Sueur*.[2] The following characteristics were ascertained :—

Origin.	Specific Gravity at 15·5° (water 15·5° = 1).	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Insoluble Acids + Unsaponifiable.	Refractive Index. Butyro-refractometer at 40° C. "Degrees."	Viscosity in Redwood's Viscometer. Seconds at 70° F.
Bombay	0·9206	180·1	108·29	0·89	—		382·8
Bengal var. rai.	0·9158	172·1	101·82	0·33	95·49	60	379·3

The optical rotations in a 200 mm. tube were −0° 25′ and −0° 18′ respectively.

Suzzi described two species of black mustard seed oil cultivated in Italian East Africa (Erythrea), viz. *Brassica nigra* and *Brassica carinata*, the seeds of which contain 29·75 and 29·74 per cent of oil respectively. The characteristics of the two oils, ascertained by *Suzzi*, are the following :—

	Oil from *Brassica nigra*.	Oil from *Brassica carinata*.
Specific gravity at 15° C. . . .	0·9175	0·917
Saponification value	176·5	175·2
Iodine Value	116·1	112·7
Maumené test	77° C.	74° C.

Fatty Acids

Melting point [3]	16·2° C.	...
Neutralisation value	179·2	179·5
Saponification value	181·1	182·0

[1] Goldschmiedt, *Wiener Berichte*, 70 [2], 451. [2] *Journ. Soc. Chem. Ind.* 1898, 991.
[3] Crossley and Le Sueur's method.

Physical and Chemical Characteristics of Black Mustard Seed Oil

Origin.	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
	15	0·916-0·920	Allen	−17·5	Chateau	174·0-174·6	De Negri and Fabris	96	Moore
	15	0·9170-0·9175	De Negri and Fabris			174·7	Blasdale	106·25-106·57	De Negri and Fabris
	15	0·9161	Blasdale			175·8	Wijs	103·07	Lengfeld and Paparelli
Bengal	15·5 (water	0·9155	Crossley and Le Sueur [2]			173·3	Crossley and Le Sueur	103·6	Blasdale [1]
Central Provinces	15·5 =1)	0·9185	,,			173	,,	105·8-113	Tolman and Munson
	,,	0·9170-0·9193	Tolman and Munson					122·3	Wijs
India	20	0·9143	Wijs					98·84	Crossley and Le Sueur
								110·51	

Physical and Chemical Characteristics of Black Mustard Seed Oil—continued

Maumené Test.		Refractive Index.			Viscosity.	
°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
44	Girard	15·5	1·4672	Tolman and Munson	425·4	Crossley and Le Sueur
42-43	De Negri and Fabris				355·4	,, ,,
58·5 (!)	Lengfeld and Paparelli	Butyro-refractometer. "Degrees."				
		15·5	76·5	Tolman and Munson		
		40	59·5	Crossley and Le Sueur		

[1] *Journ. Soc. Chem. Ind.* 1896, 206. [2] *Journ. Soc. Chem. Ind.* 1898, 991. The two samples had the acid values 7·35 and 5·72 respectively, and the optical activity, in a 200 mm. tube, −0° 17′ and −0° 30′ respectively.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Value.		Mean Molecular Weight.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer.
95·05	Crossley and Le Sueur	15·5	Girard	16 16-17 15	Girard De Negri and Fabris Blasdale	109·6 126·5	De Negri and Fabris Wijs	187·1	Wijs	299·8	Wijs
						Liquid Fatty Acids.					
						119·8	Tolman and Munson				

WHITE MUSTARD SEED OIL

French—*Huile de moutarde blanche.* German—*Weisssenföl.*
Italian—*Olio di mostarda bianca.*

For tables of characteristics see pp. 217, 218.

White mustard seed oil is obtained from the seeds of *Sinapis alba* (*Brassica alba*). The seeds contain 25-26 per cent of an oil of golden-yellow colour, and having a burning taste.

Most of the physical and chemical characteristics are almost identical with those of black mustard oil. The iodine values, however, appear to differ considerably. This agrees with *Tolman* and *Munson's* statement that this oil yields only traces of solid acids by the lead-salt-ether method. *Hehner* and *Mitchell* obtained 1·5 per cent of an ether insoluble bromide from a specimen of white mustard seed oil.

A sample examined by *Archbutt*[1] yielded 1·18 per cent of crude arachidic acid, of the melting point 69° C.

The oil is used as a burning and lubricating oil.

[1] *Journ. Soc. Chem. Ind.* 1898, 1009.

Physical and Chemical Characteristics of White Mustard Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9125-0·9160	De Negri and Fabris	−16·3	Chateau	170·3-171·4	De Negri and Fabris	92·1-93·8	De Negri and Fabris
15	0·9151	Blasdale			173·9	Blasdale	97·68	Lengfeld and Paparelli
15·5	0·914-0·916	Allen			171·2	Crossley and Le Sueur	98·4	Blasdale
15·5 (water 15·5 = 1)	0·9142[1]	Crossley and Le Sueur			174·6	Wijs	96·75	Crossley and Le Sueur
20	0·9121	Wijs					103	Wijs

Physical and Chemical Characteristics of White Mustard Seed Oil—continued

Maumené Test.		Refractive Index.			Viscosity.	
° C.	Observer.	° C.		Observer.	Seconds at 70° F.	Observer.
44·45	De Negri and Fabris	15·5	1·4750	Tolman and Munson	402	Crossley and Le Sueur
49·5	Lengfeld and Paparelli	Butyro-refractometer. "Degrees."				
		15·5	74·5	Tolman and Munson		
		40	58·5	Crossley and Le Sueur		

[1] Indian oil (*Journ. Soc. Chem. Ind.* 1898, 991); the acid value of this specimen was 5·40; its optical activity in a 200 mm. tube −0° 9′.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point. °C.	Iodine Value. Per cent.	Observer.	Neutralisation Value.		Mean Molecular Weight.	
Per cent.	Observer.				Mgrms. KOH.	Observer.		Observer.
96·7	Lengfeld and Paparelli	15-16	94·7-95·87	De Negri and Fabris Blasdale	185·8	Wijs	301·9	Wijs
95·86	Crossley and Le Sueur	16	106·2	Wijs				
			Liquid Fatty Acids.					
			103·1	Tolman and Munson				

RADISH SEED OIL

French—*Huile de raifort.* German—*Rettichöl.*
Italian—*Olio di ravano* (*ravanello*).

For tables of characteristics see p. 220.

Radish seed oil, which, like the oils described last, closely resembles rape oil, is obtained from the seeds of *Raphanus sativus*, L. (rat-tail radish), which contain from 45 to 50 per cent of oil. The green colour said to be characteristic of the soap solution of hedge mustard oil is not noticeable on saponifying the oil (*De Negri* and *Fabris*).

An Indian oil from Assam had the acid value 14·5 (*Crossley* and *Le Sueur* [1]). This specimen is described as a *non*-drying oil.

[1] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Characteristics of Radish Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.		Viscosity.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	° C.	Observer.	Butyro-refractometer at 40° C. "Degrees."	Observer.	Seconds at 70° F.	Observer.
15 (water at 15 = 1)	0·9175	De Negri and Fabris	−10 to −17·5	Schaedler	178·05	De Negri and Fabris	95·6-95·9	De Negri and Fabris	0·33	Crossley and Le Sueur	51	De Negri and Fabris	57·5	Crossley and Le Sueur	385·3	Crossley and Le Sueur
15·5 (water at 15·5 = 1)	0·9163	Crossley and Le Sueur			173·8	Crossley and Le Sueur	92·85	Crossley and Le Sueur								
20	0·9142	Wijs[1]			179·4	Wijs	112·4	Wijs								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Value.		Mean Molecular Weight.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer
95·94	Crossley and Le Sueur	13-15	De Negri and Fabris	20	De Negri and Fabris	97·1 115·3	De Negri and Fabris Wijs	189·5	Wijs	296	Wijs

[1] *Zeits. f. Unters. Nahrungs- u. Genussm.* 1903, 492.

JAMBA OIL[1]

French—*Huile de Jamba.* German—*Jambaöl.*
Italian—*Olio di Jambo.*

For tables of characteristics see p. 222.

This oil, obtained from the seeds of a plant belonging to a variety of the genus *Brassica*, is closely related to rape oil. The seeds contain about 26 per cent of oil.

The oil behaves somewhat abnormally in that it does not lend itself readily to the manufacture of "blown" oil, as the specific gravity of the oil does not rise by "blowing" at the same rate as that of other oils belonging to the rape oil group. A further instance of its abnormal behaviour is that the temperature does not rise spontaneously when the source of heat has been removed.

A sample examined in the author's laboratory contained 0·45 per cent unsaponifiable matter; it yielded 1·05 per cent of fatty acids insoluble in petroleum ether. *Thomson* and *Dunlop*[2] found 1·02 per cent of unsaponifiable matter.

Jamba oil is distinctly inferior to the rape oils made from genuine rape seed (see p. 205), and this difference finds its expression in the commercial value of the oil, which is generally twenty to thirty shillings per ton lower in price than refined colza oil.

Jamba oil is recognised by its peculiar taste and smell. It may be considered a good burning oil, but it does not burn as well as colza oil (cp. Vol. III. Chap. XV.). Jamba oil is, however, a distinctly better burning oil than ravison oil, and, in this respect, takes its place between ravison oil and best Indian rape oil.

[1] De Negri and Fabris, *Annali del Laboratorio delle Gabelle*, 1891-92, 137.
[2] *Analyst*, 1906, 282.

[TABLE

Physical and Chemical Characteristics of Jamba Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Maumené Test.		Refractive Index. Butyro-refractometer.	
15° C	° C.	Mgrms. KOH.	Per cent.	° C.	Observer.	° C.	"Degrees."
0·9150-0·9158	−10 to −12	172·26	95·2-95·6	51-53	De Negri and Fabris		
0·9151	...	174·8	102·5	...	Lewkowitsch	25	67·2
		175·3	98·3	...	Thomson and Dunlop[1]		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.	Mean Molecular Weight.	
Per cent.	° C.	° C.	Mgrms. KOH.	Per cent.		Observer.
...	16-11	19-21	173·8-174	96·1-96·2	...	De Negri and Fabris
96·52					305	Lewkowitsch

[1] *Analyst*, 1906, 282.

(3) Non-Drying Oils

The oils belonging to this class are characterised by lower iodine values than those of the two preceding classes. Linolenic acid appears to be completely absent; linolic acid seems to be present in small quantities only. Those oils which stand at the head of the list still possess slight drying properties. Owing to the predominance of olein the non-drying oils solidify on treatment with nitrous acid, yielding hard elaïdin; castor oil gives in this test solid ricinelaïdin.

It should be noted that the oils are non-drying at the ordinary temperature only; at higher temperatures they become viscous and thicken. The chemical changes then taking place have not yet been investigated.

I have placed castor oil (and also grape seed oil, which seems to be related to it) at the end of this class, on account of its being a most markedly non-drying oil. The chemical composition of castor oil (and, pending further confirmation, also of grape seed oil) differs totally from that of all other fatty oils; so that for this reason the forming of a separate group, consisting of castor oil and grape seed oil, appears to be justified.

SMALL FENNEL OIL

French—*Huile de nigelle.* German—*Schwarzkümmelöl.*
Italian—*Olio di cominella* (*nigella*).

For tables of characteristics see p. 224.

Small fennel oil is expressed in the East Indies from the seeds of *Nigella sativa*, L., and serves as an edible oil.

The sample examined by *Crossley* and *Le Sueur* had an acid value of 97·4, and yielded 88·8 per cent insoluble acids + unsaponifiable. The high acidity of the sample may explain the apparently abnormal *Reichert-Meissl* value and the low percentage of insoluble acids.

The plant is also cultivated in Italy and in Italian East Africa (Erythrea). The Erythrean seed contains 32·7 per cent of oil (*Suzzi*).[1]

According to experiments made by *Crossley* and *Le Sueur* small fennel oil is a non-drying oil.

[1] *I semi oleosi e gli olî.* Written for the Milan Exhibition, 1906.

Physical and Chemical Characteristics of Small Fennel Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.	Maumené Test.	Observer.
At 15·5° C. (water at 15·5 =1).	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refracto-meter at 49° C. "Degrees"	°C.	
0·9248	196·4	116·20	5·40	58·5	...	Crossley and Le Sueur
	192·6	123·2	...	...	89	Suzzi

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Neutralisation Value.	Saponification Value.	Observer.
°C. (Titer Test).	Mgrms. KOH.	Mgrms. KOH.	
−19 to −16	197·6	199·7	Suzzi

QUINCE OIL

French—*Huile de coing.* German—*Quittensamenöl.*
Italian—*Olio di cotogno.*

For tables of characteristics see pp. 224 and 225.

The seeds of the quince, *Cydonia vulgaris*, Pers. (cultivated in Asia and Europe), contain about 15 per cent of a fatty oil of yellow colour, and of a pleasant odour faintly resembling that of almond oil.[1] The specimen examined yielded 95·2 per cent of insoluble acids + unsaponifiable, and had the acid value 31·7.

The oil contains a liquid hydroxy acid, $C_{17}H_{32}(OH)CO_2H$, the dibromide of which melts at 108° C. (Vol. I. Chap. VIII.). The solid acids contain myristic acid and another solid acid, which has not yet been identified.

Physical and Chemical Characteristics of Quince Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.	Maumené Test.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refractometer. "Degrees."	°C.
0·922	−11 to −13[2]	181·75 187·7[2]	113 120·2[2]	0·5	68·5 (at 25° C.)	73[2]

[1] Hermann, *Arch. d. Pharm.* 1899, 237, 358.
[2] Fabris and Settimj, *Atti del VI. Congresso internaz., Roma*, v. 751.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Iodine Value.
Per cent.	°C.	°C.	Per cent.
95·5	26-27	33-34	124·6
			Liquid Fatty Acids.[1]
			132·1

CHERRY KERNEL OIL

French—*Huile de cerisier.* German—*Kirschkernöl.*
Italian—*Olio di ciliegie.*

For tables of characteristics see p. 226.

The characteristics given in the tables refer to extracted oil.

Cherry kernel oil is obtained from the kernels of the cherry (*Prunus cerasus*, L.). The kernels contain 35-36 per cent of oil. In its fresh state the oil has a golden-yellow colour and a faint odour of almonds, which it loses on becoming rancid.

With nitric acid of specific gravity 1·4 cherry kernel oil becomes dark reddish brown; with *Bieber's* reagent (p. 238) a brown colouration is obtained.

De Negri and *Fabris* found a notable quantity of hydrocyanic acid in the extracted oil.

In South Germany (Wurtemberg) the "cold-drawn" oil is used for edible purposes. The oil expressed at a higher temperature serves as a burning oil, and also for soap-making. As cherry kernel oil easily turns rancid, it is not used as an adulterant of almond oil.

[1] The proportion of liquid fatty acids was 77·3 per cent.

Physical and Chemical Characteristics of Cherry Kernel Oil

Specific Gravity.		Solidifying Point.		Saponification Value		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C	Observer.
0·9235-0·9238	De Negri and Fabris	−19 to −20	De Negri and Fabris	194·8-195	De Negri and Fabris	110·8-110·9	De Negri and Fabris	45	De Negri and Fabris
0·9285	Micko			193·4	Micko	114·3	Micko		
						113·2[1]	Tortelli and Ruggeri		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
15-13	De Negri and Fabris	19-21	De Negri and Fabris	189	Micko	296·2	Micko	114·3	De Negri and Fabris
...	...	16-20·6[2]	Micko	...	...	...	...	104·3	Micko

Liquid Fatty Acids.	
124·7	Tortelli and Ruggeri

[1] Cold pressed oil.

[2] Determined by the capillary tube method.

CHERRY LAUREL OIL[1]

French—*Huile de laurier cerise.* German—*Kirschlorbeeröl.*
Italian—*Olio di lauroceraso.*

This oil has been extracted from the kernels of the cherry laurel, *Prunus laurocerasus*, L., a tree indigenous to Persia and the Caucasus, and cultivated in Italy since the sixteenth century.

Cherry laurel oil has a golden-yellow colour; its odour resembles that of bitter almonds. This oil, like the preceding one, contains appreciable quantities of hydrocyanic acid.

Physical and Chemical Characteristics of Cherry Laurel Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.	Maumené Test
At 15° C.	°C.	Mgrms. KOH.	Per cent.	°C.
0·9230	−19 to −20	194	108·9	44·5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
17-15	20-22	112·1

APRICOT KERNEL OIL

French—*Huile d'abricotier.* German—*Aprikosenkernöl.*
Italian—*Olio di albicocche* (*Olio di armelline*).

For tables of characteristics see p. 228.

Apricot kernel oil is obtained from apricot kernels (*Prunus armeniaca*, L.), which contain from 40 to 45 per cent of oil.

The freshly expressed oil is almost colourless; on keeping it becomes yellow.

With nitric acid, spec. grav. 1·4, apricot kernel oil assumes an orange colour. With *Bieber's* reagent (p. 238) a peach-blossom colour is obtained; this is so characteristic of the oil, that by means of this colour reaction apricot kernel oil is identified, and can be detected if present in almond oil in large quantities.

[1] De Negri and Fabris, *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 173.

Physical and Chemical Characteristics of Apricot Kernel Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index. Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At °C.	"Degrees."	Observer.
15	0·9191	Valenta	−20	Maben	192·2-192·9	De Negri and Fabris	101	De Negri and Fabris	0·00	Crossley and Le Sueur	46	Girard	25	65·6	Beckurts and Seiler
15	0·9204	Maben									42·5	De Negri and Fabris			
15·5 (water at 15·5 = 1)	0·9195 [1]	Crossley and Le Sueur			193·11	Micko	108	Micko					25	66·6	Mansfeld
	0·9172 [5]	Lewkowitsch			192·9	Valenta	96·02	Crossley and Le Sueur					40	57·5 [1]	Crossley and Le Sueur
	0·9200 [4]				188 [1]	Crossley and Le Sueur	104·2-104·7 [3]	Tortelli and Ruggeri					40	58·0 [4]	Lewkowitsch
90	0·901-0·9015	Dieterich			198·2 [5]	Lewkowitsch	100·1 [4]	Wijs					40	57·0 [5]	,,
					190·3-192·4 [4]	,,	107·4-108·7 [4]	Lewkowitsch					50	52·25	Dieterich
							107·9	,,					20	1·4712	Harvey

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index. Butyro-refractometer.		
Per cent.	Observer.	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At °C.	"Degrees."	Observer.
95·40 [1]	Crossley and Le Sueur	15	0·9195	Dieterich	0	Hübl	4·5	Hübl	194	Micko	288·6	Micko	103·8	De Negri and Fabris	25	56·3	Dieterich
		90	0·8875	,,			2·3 } 3·5 }	De Negri and Fabris					102·6	Micko	40	56·0	,,
							13·4-18 [2]	Micko					99·4	Dieterich	50	41·3	,,
													Iodine Value Liquid Fatty Acids.				
													111·1-111·8 [3]	Tortelli and Ruggeri			

[1] Oil from the Punjab. [2] Determined in a capillary tube. [3] Cold-pressed oil, eighteen months old. [4] Californian oil. [5] Mogador oil.

The deep red colouration obtained on shaking the oil with an ethereal solution of phloroglucinol (one-tenth per cent solution) is not so characteristic of the oil, since some almond oils (see p. 238) give the same colour reaction.[1] It should also be noted that the colour reaction is much stronger in the case of fresh oils than with samples that have been kept for half a year and longer.

A sample of extracted oil examined by *Micko* had the acid value 0·64. A three months' old sample examined by *Lewkowitsch* had the acid value 2·8.

Apricot kernel oil is used as an edible oil; in perfumery it is employed for adulterating or wholly substituting almond oil. Apricot kernel oil forms an important article of commerce. The commercial "almond oil, French," is practically pure apricot kernel oil, or a mixture of apricot kernel and peach kernel oils (cp. p. 231).

PLUM KERNEL OIL

French—*Huile de prunier.* German—*Pflaumenkernöl.*
Italian—*Olio di susino, olio di prugne.*

For tables of characteristics see p. 230.

The characteristics given in the tables refer both to expressed and extracted oils.

Plum kernel oil is obtained from the kernels of plums (*Prunus domestica*, L., and *Prunus damascœna*, L.). The oil is light yellow in colour, and possesses an agreeable, mild, almond-like taste. *Fabris* and *Settimj*[2] obtained, by extracting the kernels with petroleum ether, 25 per cent of an oil which yielded 70 per cent of liquid fatty acids.

With nitric acid, of specific gravity 1·4, plum kernel oil assumes an orange colour (like apricot kernel oil). With *Bieber's* reagent, consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water, a pink colouration is obtained.

The sample examined by *Micko* had the acid value 0·55.

The oil is chiefly used to adulterate almond oil.

[1] Lewkowitsch, *Analyst*, 1904, 106.
[2] *Atti del VI. Congresso, etc.*, Roma, 1907, Vol. V. 759.

Physical and Chemical Characteristics of Plum Kernel Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Butyro-refractometer. "Degrees."	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 25° C.	Observer.
0·91949	De Negri and Fabris	−5 to −6	De Negri and Fabris	191·48	De Negri and Fabris	100·4	De Negri and Fabris	44·5-45	De Negri and Fabris	63·1	F. and S.
0·9160	Micko [1]	−10	Fabris and Settimj	191·55	Micko	100·2	Micko				
				189·1	F. and S.	93·3 [3]	Tortelli and Ruggeri				
						91·2	F. and S.				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
96·2	Fabris and Settimj	15-13	De Negri and Fabris	20-22	De Negri and Fabris	200·47	Micko	279·3	Micko	102	De Negri and Fabris
		12-13	F. and S.	12·14-18·1 [2]	Micko		...	...	...	104·2	Micko
										95·7	F. and S.
										Liquid Fatty Acids.	
										98·6 [3]	Tortelli and Ruggeri
										102·2	F. and S.

[1] *Journ. Soc. Chem. Ind.* 1893, 935.

[2] Determined in a capillary tube.

[3] Cold-pressed oil, eighteen months old.

PEACH KERNEL OIL

French—*Huile de pêcher.* German—*Pfirsichkernöl.*
Italian—*Olio di pesche, Olio di pesco.*

For tables of characteristics see p. 232.

Peach kernel oil (peach oil) is obtained from the kernels of the peach (*Prunus persica*, Sieb. et Zucc.). They contain 32-35 per cent of a pale yellow oil, which greatly resembles almond oil. *Dieterich* states that the freshly expressed oil—of which he obtained 10-12 per cent from the kernels—smells slightly of hydrocyanic acid.[1] A sample examined by *Lewkowitsch* had the acid value 3·0. With nitric acid of the specific gravity 1·4, peach kernel oil becomes first yellowish brown, afterwards dirty orange. With *Bieber's* reagent it remains unchanged at first,[2] then after about half-an-hour's standing it becomes slightly pink, the pink colour being less strongly developed than is the case with apricot kernel oil. In the phloroglucinol test (see p. 238) peach kernel oil, like apricot kernel oil, gives a red colouration.

This oil is chiefly used for adulteration, or for substitution, of almond oil. The commercial "almond oil, French," is frequently a mixture of peach kernel oil with apricot kernel oil (cp. p. 229).

Peach kernel oil is adulterated in its turn with poppy seed oil; in some cases commercial "peach kernel oil" consisted of hazelnut oil (*Bennett*[3]).

The seeds from *Prunus Brigantiaca*, Vill., grown in the south-east of France, furnish on expression the commercial "huile de marmotte."

[1] This is confirmed by Fabris and Settimj. The oil obtained by these observers gave 84·5 per cent of liquid fatty acids.

[2] Lewkowitsch, *Analyst*, 1904, 106.

[3] *Chemist and Druggist*, 1908, 89.

[TABLE

Physical and Chemical Characteristics of Peach Kernel Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.					
											Butyro-refractometer.			Oleo-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At °C.	"Degrees."	Observer.	At °C.	"Degrees."	Observer.
15	0·918	De Negri and Fabris	Below −20	Maben	189·1	Maben	92·5-93·5	De Negri and Fabris	42-43	De Negri and Fabris	25	67·2 [1]	Dieterich	22	+7·5 to +11·5	Pearmain
15	0·92147	Micko			192·5	De Negri and Fabris	99·7	Micko			,,	65·7 [2]	,,			
15·5	0·9198	Lewkowitsch			191·1	Micko	109·7 [1]	Dieterich			,,	66·1	Beckurts and Seiler			
90	0·8899	Dieterich			191·4	Lewkowitsch	98·6 [2]	,,			,,	66·5	Mansfeld			
							94·8 [3]	Tortelli and Ruggeri			40	58·5 [1]	Dieterich			
											,,	57·0 [2]	,,			
							110·1	Wijs			,,	57·5	Lewkowitsch			
							95·24	Lewkowitsch			50	52·2 [1]	Dieterich			
											,,	51·5 [2]	,,			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
94·0	Fabris and Settimj	Titer Test.		3-5	De Negri and Fabris	209·9	Micko	278·8	Micko	94·1	De Negri and Fabris
						205·0	Lewkowitsch				
		13-13·5	Lewkowitsch	10-18·9	Micko	...	...	...	...	101·9	Micko
										98·5	F. and S.
										Liquid Fatty Acids.	
										101·9	Tortelli and Ruggeri
										104·1	F. and S.

[1] Freshly prepared oil. [2] Old oil. [3] Cold-pressed oil, eighteen months old.

ALMOND OIL

French—*Huile d'amande.* German—*Mandelöl.*
Italian—*Olio di mandorle.*

For tables of characteristics see pp. 235-237.

Almond oil is obtained from the seeds of *Prunus amygdalus*, Stokes (*Amygdalus communis*, L.). The commercial oil is expressed [or extracted] chiefly from bitter almonds, the seeds of *Prunus amygdalus*, var. *amara*. Bitter almonds contain amygdaline, and a ferment (emulsin) which, acting on the amygdaline, gives rise to the formation of benzaldehyde, glucose, and hydrocyanic acid. Hence the press-cakes from almond oil production find a profitable outlet in the manufacture of genuine "ethereal bitter almond oil" by triturating the meal with water.

The sweet almonds (from *Prunus amygdalus*, var. *dulcis*) are but rarely used alone for the preparation of almond oil. Mogador bitter almonds, which are largely used in this country for the manufacture of almond oil, are always more or less mixed with sweet almonds.

The oils obtained from both varieties are practically identical, so that no definite difference can be established by chemical means; this will be seen by a glance at the accompanying table. Nor can a definite difference be established botanically between the two varieties "amara" and "dulcis." The principal countries from which almonds are supplied are Morocco, the Canary Islands, Portugal, Spain, France, Italy, Sicily, Syria, and Persia.

Sweet almonds yield more oil than do bitter almonds. The former give from 44 to 55 per cent of oil, whereas the latter may fall in their content of oil to 20 per cent. On an average bitter almonds yield from 38 to 45 per cent of oil.

Almond oil is, according to *Gusserow*, free from stearin; this is confirmed by *Hehner* and *Mitchell*.[1] The glycerides in almond oil consist chiefly of olein; the high iodine value points, however, to the presence of glycerides of fatty acids belonging to a less saturated series than the oleic. Indeed, *Farnsteiner* has isolated from the mixed fatty acids linolic tetrabromide in a quantity corresponding to 5·79 per cent of linolic acid.

Contrary to older statements, almond oil does not easily turn rancid. A number of genuine almond oils, 12 to 18 months old, examined in my laboratory, had acid values varying from 0·79 to 5·1 (see table, p. 239).

Almond oil is largely used in pharmaceutical practice, hence the Pharmacopœia of the different countries prescribe certain reactions

[1] *Analyst* 1896, 328.

for identification. Most of these, such as the specific gravity test and the elaïdin test, are of very little use for purposes of identification. Of greater importance is the determination of the melting point of the mixed fatty acids, almond oil being characterised by the low melting point of its mixed fatty acids. According to the German Pharmacopœia the mixed fatty acids of pure almond oil should remain liquid at 15° C. for an indefinite length of time; mixed with an equal volume of alcohol they should give a clear solution at 15° C., and not become turbid on adding twice the volume of alcohol. *Olive*, *sesamé*, *arachis*, and *cotton seed oils* may thus be detected. *Apricot* or *peach kernel oils* will, however, escape detection.

Older statements that almond oil is adulterated with the following oils: poppy seed, walnut, cotton seed, sesamé, arachis, olive, lard oils, hardly hold good in the case of the almond oils found in commerce to-day. It need, therefore, only be briefly pointed out that poppy seed, walnut, cotton seed, and also sesamé oils would be detected by a higher iodine value than the normal one. The confirmatory tests to be applied would be :—in the case of cotton seed oil, the *Halphen* colour test, and especially the melting point of the mixed fatty acids; and in the case of sesamé oil, the *Baudouin* colour reaction. Arachis oil would be identified by the isolation of arachidic acid; olive oil by the high melting point of the fatty acids, and the solidifying point of the oil itself; lard oil by the phytosteryl acetate test.

The chief adulterants of almond oil are apricot kernel oil and peach kernel oil. These latter are used to such an extent, that frequently they completely substitute almond oil; indeed "foreign" almond oil, or "oil of sweet almonds, French," *Oleum Amygdalarum Gallicum*, is nothing else but a mixture of apricot kernel oil and peach kernel oil. Genuine almond oil is sold commercially under the name "almond oil, English." Pure almond oil may be differentiated from apricot and peach kernel oils by its lower iodine value, so that an almond oil having an iodine value exceeding 105 must be looked upon with suspicion. The differentiation of almond oil from these two oils by means of the colour tests described below will not lead to decisive results in every case, owing to the different behaviour of almond oils from various sources.

The close relationship in which apricot kernel and peach kernel oils stand to almond oil renders detection of these in an almond oil a very difficult problem, which cannot be solved with certainty in the present state of our knowledge, since most of the physical and chemical characteristics, including the iodine value, fail to reveal the presence of the kernel oils.

In doubtful cases recourse may be had to the following colour reactions, which should, however, be looked upon as confirmatory tests only, and as more suitable for differentiating peach kernel and apricot kernel oils severally from almond oils than for detecting the former oils when they are admixed with almond oil.

Physical and Chemical Characteristics of Almond Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
12	0·9168 [1]	Mills and Akitt	−10	Girard	195·4	Valenta	98·4	Hübl
,,	0·9154 [2]	,,	−21	Maben	190·9	Dieterich	96·6-99·2	Beringer
15	0·917-0·920	Chateau			190·5-191·2 [2]	De Negri and Fabris	96·2-101·9	Dieterich
,,	0·914-0·920	Allen						
,,	0·9180	Maben			189·5-191·7 [1]	,,	97·5	Del Torre
,,	0·9186	Valenta					98-99	Peters
,,	0·9183	Massie					98·4 [2]	Moore
,,	0·9190	Del Torre					93-95·4 [2]	De Negri and Fabris
,,	0·9190-0·9195 [2]	De Negri and Fabris					94·1-96·5 [1]	,,
,,	0·9175-0·9195 [1]	,,					95·8 [2]	Tortelli and Ruggeri
,,	0·9177-0·9185	Allen and Brewis					95·8-101·26	Allen and Brewis
15·5	0·9186	Tolman and Munson					98·5-100·2 [2]	Lewkowitsch
,	0·9178-0·9183	Lewkowitsch						

[1] From bitter almonds.

[2] From sweet almonds.

Physical and Chemical Characteristics of Almond Oil—continued

Thermal Tests.				Refractive Index.		
Maumené Test.		Heat of Bromination.				
°C.	Observer.	°C.	Observer.	At °C.		Observer.
52-54	Maumené	17·6	Hehner and Mitchell	15·5	1·4728	Tolman and Munson
53	Del Torre			20	1·4705	Harvey
51-52 [2]	De Negri and Fabris [3]	20·25	Bromwell and J. L. Meyer	60	1·4555	Thoerner
51-53 [1]	,,	20·6-21	Allen and Brewis	Oleo-refractometer.		
				"Degrees."		Observer.
				+ 6		Jean
				+ 7		Bruyn and van Leent
				+8 to + 10·5 at 22° C.		Pearmain
				Butyro-refractometer.		
				At °C.	"Degrees."	Observer.
				15·5	70·9	Tolman and Munson
				25	64·8	Beckurts and Seiler
				,,	64·0	Dieterich

[1] From bitter almonds. [2] From sweet almonds. [3] Jean's thermelæometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
Titer Test.		14	Hübl	204	Thoerner	93·5-95·5 [2]	De Negri and Fabris	1·4461	Thoerner
9·5-10·1 [2]	Lewkowitsch	13-14 [1&2]	De Negri and Fabris			94·1-96·5 [1]	,,		
11·3-11·8 [1]	,,					Liquid Fatty Acids.			
						101·7 [2]	Tortelli and Ruggeri		

[1] From bitter almonds.

[2] From sweet almonds.

The Nitric Acid Test.—Almond oil, on being shaken with nitric acid of specific gravity 1·4, remains colourless, or becomes only slightly yellow, whereas apricot kernel oil assumes an orange-yellow colour, and peach kernel oil becomes yellowish brown, subsequently passing into a dirty-orange colour.

Bieber's Test is carried out by agitating five volumes of oil with one volume of a mixture consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water. Pure almond oil does not change its colour, whereas apricot kernel oil gives a pink (peach-blossom) colour, and peach kernel a faint pink colouration after standing for some little time. I find that it is necessary to prepare *Bieber's* reagent fresh for each set of tests; it should also be noted that the colour reaction is much more distinct in the case of freshly expressed oil than in the case of a sample which has been kept for half a year and longer (*Lewkowitsch*).

Whereas it is thus possible to differentiate broadly almond oil from apricot and peach kernel oils, it would be hazardous to pronounce adulteration on the strength of these colour tests alone. Mixtures of almond oil and apricot kernel oil containing one-half of the latter still show distinctly the colour reaction of the latter, but mixtures containing 25 per cent of apricot kernel oil can no longer be detected with certainty (*Lewkowitsch* [1]).

Recently, a $\frac{1}{10}$th per cent solution of phloroglucinol in ether, applied in the presence of nitric acid, has been proposed as a test for apricot kernel and peach kernel oils.[2] Nitric acid of specific gravity 1·45 gives, in my experience, better results than the acid of 1·42 specific gravity recommended by *Chwolles*. Undoubtedly apricot kernel oil and peach kernel oil give distinct deep red colourations with the reagent, in contradistinction to some almond oils; yet other specimens of genuine almond oils tested by me (see table, p. 239) show the same reaction more or less strongly. This test must, therefore, be employed with even greater circumspection than the *Bieber* test.

In the following table I have collated a number of tests carried out with genuine almond oils. On comparing the numbers with those given for apricot and peach kernel oils, they will, in doubtful cases, render some assistance to the analyst.

[1] *Analyst*, 1904, 106.

[2] Chwolles, *Pharm. Zeit.* 1903, 109. The reagent was first proposed by Kreis. Cp. Fahrion, *Zeit. f. ang. Chem.* 1904, 869.

[TABLE

Characteristics of some Almond and Allied Oils (Lewkowitsch)

Description of Oil.	Specific Gravity.	Saponification Value.	Iodine Value.	Butyro-refractometer at 40° C.	Acid Value.	Fatty Acids.		Colour Reactions.	
						Neutralisation Value.	Saponification Value.	Bieber's Test.	Phloroglucinol Test.
Almond Oils, expressed from—				"Degrees."					
1. Valencia Sweets . . .	0·91995	207·6	99·4	57·5	5·16	207·8	207·6	Colourless	No colouration
2. Blanched Valencia Sweets .	0·9182	191·7	103·6	57·5	2·9	196·4	201·7	,,	No crimson colouration
3. Sicily Sweets . . .	0·9178	183·3	100·3	57·0	0·79	198·8	202·2	,,	,, ,,
4. Mazagan Bitters . . .	0·9180	188·6	102·5	56·5	3·1	196·8	203·1	,,	Slightly crimson
5. Small Indian Almonds .	0·91907	189·2	96·65	57·0	2·9	195·8	200·7	,,	,, ,,
6. Mogador Bitters . . .	0·9183	194·98	104·2	57·0	1·3	197·1	203·2	,,	No crimson colouration
7. Peach Kernel Oil	0·9198	191·4	95·24	57·5	3·0	196·8	205·0	Colourless at first, then pink	Deep crimson ,,
8. Apricot ,, ,, ...	0·9200	192·4	107·4	58·0	2·3	198·0	202·0	Pink colouration	,, ,, ,,
9. ,, ,, ,, from Mogador Kernels	0·9172	198·2	107·9	57·0	2·8	194·0	200·7	Slightly pink	Less deep crimson than 8
10. Californian Apricot Kernel Oil .	0·92026	190·3	108·7	58·0	1·2	197·8	202·8	Very slightly pink	,, ,, ,,

The following numbers, representing the refractive indices of the ten oils for different rays, have been determined by *Ross*;[1] unfortunately, the numbers given below do not furnish an analytical means of differentiating almond oil from the related oils.

Refractive Indices at 20 *Degrees Centigrade* (*Ross*)

Oil	D	C	F	G
No. 1	1·4715	1·4688	1·4780	1·4835
,, 2	1·4715	1·4688	1·4780	1·4836
,, 3	1·4711	1·4685	1·4777	1·4833
,, 4	1·4712	1·4686	1·4778	1·4834
,, 5	1·4710	1·4685	1·4777	1·4833
,, 6	1·4714	1·4688	1·4780	1·4835
,, 7	1·4710	1·4685	1·4776	1·4832
,, 8	1·4717	1·4692	1·4784	1·4839
,, 9	1·4715	1·4690	1·4782	1·4837
,, 10	1·4725	1·4700	1·4792	1·4847

Almond oil is far too expensive to admit of any other use than in pharmaceutical practice. Statements in the technical literature and even in patent specifications as to the employment of almond oil in the manufacture of oil varnishes must, therefore, be accepted with the greatest reserve. Although its price would not militate against its use as a lubricating oil for fine machinery, it cannot be recommended for this purpose.

WHEAT-MEAL OIL

French—*Huile de farine de froment.* German—*Weizenmehlöl.*
Italian—*Olio di farina di frumento.*

This oil is extracted from wheat flour.[2] It must not be confounded with wheat oil. The proportion of fat in ten samples of wheat meal examined by *Plücker*[3] varied from 0·99 to 1·63 per cent.

Physical and Chemical Characteristics of Wheat-Meal Oil

Specific Gravity at 100° (water 15° C. = 1).	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Refractive Index. At 25° C.	Observer.
0·9068	166·5 (?)	2·8	101·5	1·4851	Spaeth
				Butyro-refracto-meter. "Degrees."	
				92	,,
...	182·8	...	...	...	De Negri and Fabris
...	...	2·95-4·95[4]	96·1-112·5[4]	92	Plücker

[1] *Analyst*, 1904, 106. [2] Spaeth, *Analyst*, 1896, 234. Cp. *Chem. Revue*, 1904, 127.
[3] *Zeit. f. Unters. Nahr. u. Genussm.* 1907, xiv. 751.
[4] Minimum and maximum numbers of ten samples.

SANGUINELLA OIL.[1] DOGWOOD OIL

French—*Huile de cornouiller.* German—*Hartriegelöl.*
Italian—*Olio di sanguinella.*

This oil is obtained from the seeds of the dogwood (cornel tree), *Cornus sanguinea*, L., which contain 55 per cent of oil. The oil has a greenish-yellow colour and an odour similar to that of low-grade olive oil. It is used as a burning oil, and for soap-making.

Physical and Chemical Characteristics of Sanguinella Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.
0·921	−15	192·05	100·8	52

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.	Iodine Value. Per cent.
31-29	34-37	195·1	102·75

ACORN OIL[2]

French—*Huile de gland.* German—*Eicheckernöl; Eichelöl.*
Italian—*Olio di ghiande.*

This oil is obtained by extracting the fruit of *Quercus agrifolia*; it is a deep-brown fluorescent oil. On long standing it deposits "stearine."

Physical and Chemical Constants of Acorn Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponification Value.	Iodine Value.	Maumené Test. °C.	Refractive Index.
0·9162	10	199·3	100·7	60[3]	1·4731

The melting point of the fatty acids is 25° C.

[1] De Negri and Fabris, *Annali*, etc., 181.
[2] Blasdale, *Journ. Soc. Chem. Ind.* 1896, 206. [3] Jean's thermelæometer.

CALIFORNIAN NUTMEG OIL[1]

French—*Huile de Noix de Californie.* German—*Kalifornisches Muskatöl.* Italian—*Olio di Noci di California.*

Californian nutmeg oil is obtained from the fruit of *Tumion californicum.*

Physical and Chemical Characteristics of Californian Nutmeg Oil

Specific Gravity at 15° C	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.	Refractive Index.
0·9072	191·3	94·7	77[2]	1·4766

The melting point of the fatty acids is 19° C.

OWALA OIL.[3] FULLA PANZA OIL.[4] ATTA SEED OIL

French—*Huile d'Owala.* German—*Owala Öl.* Italian—*Olio di Owala.*

For tables of characteristics see p. 243.

This oil is obtained from the seeds[4] of *Pentaclethra macrophylla*, Benth., a *Mimosea* growing on the West Coast of Africa.[5] The seeds, termed by the natives "owala," "opachala," or "atta beans," have the form of a mussel. They consist of 20·6 per cent of husks and 79·4 per cent of kernels. The weight of the whole seeds varies from 8 to 20 grams. The seeds yield 30·4 per cent, and the kernels 41·6 per cent of oil.

The oil (extracted with ether) has a faint yellowish colour, pleasant taste, and aromatic odour. The acid value of the specimen examined by *Wedemeyer* was 9, and the proportion of unsaponifiable matter 0·54 per cent.

A specimen of oil prepared by the natives, and supplied to the author through reliable sources, yielded on examination in his laboratory by the lead-salt-ether method, in two experiments, 24·7-28·60 per cent of liquid acids and 70·2-74·8 per cent of solid acids. The mean molecular weights of the latter acids were 320 and 346 respectively. From the solid acids an acid of the melting point 78°-79° C., crystallising in white laminæ, was isolated. This oil contained 2·74 per cent of unsaponifiable matter. Oil prepared in the author's laboratory from the seeds by extraction with ether yielded 2·50 per cent of unsaponifiable matter.

[1] Blasdale, *Journ. Soc. Chem. Ind.* 1896, 206. [2] By Jean's thermelæometer.
[3] Wedemeyer, *Chem. Rev.* 1906, 210; *Bulletin Imperial Institute*, 1907, p. 10.
[4] The native name for the seeds and the oil is Fulla Panza seeds and Fulla Panza oil.
[5] E. Drabble, *Quart. Journ. Inst. of Comm. Research* (Liverpool University), 1907, April; cp. "Dika Oil."

Physical and Chemical Characteristics of Owala Oil

	°C.	Specific Gravity.	Solidifying Point °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.	Refractive Index.		Observer.
	25	0·9119	4 "Stearine" separates at 18° to 19°; becomes a buttery mass at 8°.	...	186	99·3	100°	40° C.	1·4654	Wedemeyer
								Butyro-refractometer. "Degrees."		
								40° C.	59·2	,,
	100	0·8637	8	...	...	94·3	...	...	...	Imperial Institute
Native oil . .	40 (water at 15° C. = 1)	0·9036	15·5-20·6	22-24·5	167·6	...	...	...	...	Spiegel[1]
Extracted oil .	40 (water at 15° C. = 1)	0·9041	...	...	169·3	...	...	...	...	,,
						98·4	...	...	...	Warburton[1]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.	Observer.
95·6	52·1	53·9 (capillary tube)	185·7	Wedemeyer
94·2	...	52·4	...	Imperial Institute

[1] Determined in the author's laboratory.

ARACHIS OIL, PEANUT OIL, EARTHNUT OIL, GROUND NUT OIL

French—*Huile d'arachide.* German—*Arachisöl, Erdnussöl.*
Italian—*Olio di arachide.*

For tables of characteristics see pp. 249-251.

Arachis oil is obtained from the earthnuts, the seeds of *Arachis hypogœa*, L. (*Leguminosæ*).

The cultivation of the arachis nut dates back so far in history that its origin cannot be located with certainty; but it is generally assumed that the original home of the arachis nut is Brazil.

The arachis plant is chiefly cultivated[1] in the East Indies, Java, Mozambique, the West Coast of Africa (latterly in Togo and Southern Nigeria), Spain, the United States of America (chiefly in Virginia, Georgia, Tennessee, and North Carolina), La Plata, and also in the following West Indian Islands:—Trinidad, Grenada, Carriacou, St. Vincent, St. Lucien, Santa Lucia, Barbadoes, St. Kitts. The East Indian and the West African nuts represent two distinct varieties. The Indian (Bombay and Coromandel) and Mozambique earthnuts are usually decorticated before shipment to Europe. As these nuts undergo some detrimental changes on the voyage, they cannot be used for the production of best edible oil, and are mainly worked up for soap oils. The nuts coming from the Coromandel coast are wholly worked up for soap oil; those from Bombay yield oil of somewhat better quality, which can be used as a lubricating oil, for oiling wool, etc. The Mozambique nuts yield an edible oil of inferior quality, as only those seeds which are imported in their shells furnish the finest edible oils.

The arachis nuts grown in the United States are almost exclusively worked up for edible oil. The home-grown seeds do not suffice for the demand, and therefore large quantities of arachis nuts must be imported. Since decorticated nuts would be useless to the American oil manufacturer (owing to the changes they undergo during the voyage), arachis nuts are imported exclusively in the shell from the West Coast of Africa. The largest arachis nuts are obtained from the plants cultivated in Fiji.

The chief producer of arachis nuts is Senegal. The quantities shipped to Europe are set out in the following table:—

[1] With regard to the diseases of the arachis plant, cp. A. Zimmermann, *Der Pflanzer*, 1907, v. 125.

[TABLE

Exports of Arachis Nuts in Shells from Senegal

Double (metric) hundredweights

From	1900.		1901.		1902.		1903.		1904.		1905.	
	Total Exports.	Chief Destinations.	Total Exports.	Destinations.	Total Exports.	Destinations.	Total Exports.	Destinations.	Total Exports.	Destinations.	Total Exports.	Destinations.
Rufisque et Cayor	1,063,457	France . . 814,021 Holland . 111,105 Germany . 76,691 Belgium . 28,388 Denmark . ..	893,562	608,832 148,571 83,640 38,886 ..	715,016	478,992 112,082 108,735 .. 14,430	867,192	588,752 152,009 103,439 41,470 ..	750,279	440,361 165,619 77,462 45,666 ..	561,267	379,599 124,027 45,998 7,107 ..
Galam . .	3,620	France . . 3,620	230	230	4,000	4,000	2,250	2,250	..	..	9,290	9,290
Petite-Côte .	328,054	France . . 305,387 Holland . 8,870 Belgium . 5,593 Denmark . ..	324,091	283,683 21,044	355,889	326,160 21,729	531,097	459,021 52,416	595,016	464,792 77,652 .. 34,951	355,068	273,326 56,639 19,657 ..
Casamanca .	13,447	France . . 9,571 England and Colonies 3,036 Germany . ..	11,050	9,696 1,354 ..	27,337	27,336	76,723	72,999 11,162 ..	32,369	28,225 .. 4,148	33,282	33,087 .. 195
Other regions	630	France . . 630 England . ..	5,891	3,049 ..	3	.. ..	11,162	.. 11,162	168	.. 168	2,837	.. ..
Total . .	1,409,208	..	1,234,824	..	1,102,245	..	1,488,424	..	1,377,832	..	961,745	

The value of the arachis nuts exported from the Gambia Colony and Protectorate in 1906 was £278,055.

The chief centres of the arachis oil industry are Marseilles, Bordeaux, Dunkirk, Valencia, Trieste, and Delft.

The quantities of arachis nuts imported into France and Marseilles in particular are set out in the following table :—

Imports of Arachis Nuts into France and Marseilles

Kilograms

Year.	In Shells.		Decorticated.	
	France.	Marseilles.	France.	Marseilles.
1896	54,252,365	27,680,697	48,884,155	45,199,413
1897	61,440,732	30,414,186	6,959,204	6,753,230
1898	93,684,247	59,412,500	4,764,114	4,763,984
1899	94,495,450	60,685,291	11,786,721	7,232,671
1900	134,266,526	81,050,270	24,295,979	22,520,879
1901	120,408,208	72,092,808	58,132,221	54,486,709
1902	104,944,350	61,649,228	119,451,509	110,814,639
1903	146,888,425	94,116,177	100,339,519	86,223,015
1904	134,658,090	81,961,845	110,067,445	99,392,359
1905	102,900,986	57,106,499	100,746,178	97,092,561
1906	109,871,900	72,927,138	114,210,900	110,729,835

It will be seen that Marseilles receives more than half the arachis nuts (both in shells and decorticated) exported from the West Coast of Africa. The nuts are classed according to their quality as follows :—

Rufisque Cayor . . .	Senegal.
Nianing	,,
Sine	,,
Saloum	,,
Gambia	English Colony.
Casamanca . . .	French Colony.
Rio-Nunez . . .	French Guinea.

The following data are taken from actual experience on a large scale in south of Europe oil mills. Arachis nuts in shells coming from Rufisque, Saloum, Sine, Gambia—termed in the trade "haut de côte"—contain 35-36 per cent of oil; the kernels alone contain 50-51 per cent. On a large scale the nuts yield 28-30 per cent of shells and 31·5-32·5 per cent of oil, the press-cakes retaining from 8 to 9 per cent of oil. Calculated on the kernels, they yield 44·5-45·5 per cent of oil.

The Casamanca nuts—termed in the trade "bas de côte"—contain 34-35 per cent of oil, and the kernels 50 per cent. On a large scale they yield 30-32 per cent of shells and 30·5-31·5 per cent of oil.

The decorticated Bombay and Coromandel nuts contain 42 to 44 per cent of oil. On a large scale they yield 36 to 38 per cent of oil.

The decorticated Mozambique nuts contain 46 to 48 per cent of oil, and yield on a large scale 40 to 42 per cent.

The nuts are first shelled, if necessary, by special machinery, and the inner or red skin which surrounds the kernel is removed as completely as possible by a blast of air, in a manner similar to that employed for cleaning wheat in flour-mills. The husks are as a rule blown into the boiler-house to serve as fuel, or are ground and mixed with the arachis meal. The inner skins are added to the refuse meal, and are thus expressed. The separated and cleaned kernels are then ground and subjected to hydraulic pressure. Since the kernels contain from 43 to 45 per cent of oil, expression of the oil is carried out in two stages, as described in Chap. XIII. Frequently the meal is expressed three times. The first expression takes place at the ordinary temperature, the second at a temperature of 30° to 32° C., and the third at 50° to 55° C.

The "cold drawn oil" of the first expression is nearly colourless, and has a pleasant taste resembling the flavour of kidney beans. It is used as salad oil, and sold under the name "huile surfine" de Rufisque, Gambia, Sine, etc. The oil obtained by second expression also serves for edible purposes or for burning. The third quality, expressed at the highest temperature, is chiefly used for soap-making. This oil is somewhat thick and turbid, and must therefore be filtered to render it bright.

A comparison of specific gravities and iodine values of different arachis oils of first expression and second expression has been given by *Wijs*.[1] For edible purposes the oil is required to be almost water white and is hence filtered over fuller's earth or charcoal (cp. Vol. III. Chap. XV., "Edible Oils"). It should be noted that arachis oil is usually pressed in the same establishment as is sesamé oil, and since it is impossible to keep presses and press cloths separate for each kind of oil, commercial arachis oil contains a sufficient amount of sesamé oil to give the colour reaction of the latter faintly. Due regard should be had to this fact in judging a commercial sample of arachis oil which gives a faint *Baudouin* reaction.[2]

The cakes serve as an excellent cattle food.[3] The arachis cakes contain the highest amount of proteins of all known oil-cakes; moreover, these proteins are more easily digested than those of other cakes. The cakes from non-decorticated nuts contain 5·35 per cent of nitrogen and 0·9 per cent of phosphoric acid; those from decorticated nuts contain 7·9 per cent of nitrogen and 1·35 per cent of phosphoric acid. The cakes from damaged or mouldy seeds serve as a valuable fertiliser in the south of France and in Italy.

On standing at a little above 0° C. arachis oil deposits "stearine." Owing to the arachin which this "stearine" contains, it does not readily settle out as a crystalline mass. A number of experiments I have carried out[4] show that even when crystals are once obtained,

[1] Wijs, *Zeit. f. Unters. Nahrungs- u. Genussm.* 1903, 492.
[2] Cp. also Fendler, *Zeit. f. Unters. Nahrungs- u. Genussm.* 1903, 411.
[3] See Appendix.
[4] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1903, 592.

the very slight rise of temperature caused by handling the material suffices to either melt the crystalline mass, or to convert it into a gelatinous form, which withstands all attempts at filtering.

On allowing the separated "stearine" to settle out by prolonged standing in the cold, an arachis oil less rich in solid glycerides can be drawn off from the separated stearine. A "margarine d'arachide" of the iodine value 79·4, melting point 21·5° C., most likely represents the "stearine" so obtained on a large scale.[1]

Palmitic acid, stated by *Caldwell*[2] to occur in arachis oil, could not be detected by *Kreiling*,[3] who has, however, not adduced absolute proof of its absence. The latter chemist has shown that besides arachidic acid (melting point 74·5° C.), as proved by *Gössmann's* researches, another solid fatty acid, of the melting point 81° C., viz. lignoceric acid, occurs in combination with glycerol. Lignoceric acid, being less readily soluble in alcohol than arachidic acid, may be separated from the latter by means of this solvent (cp. below). The occurrence of stearic acid amongst the solid fatty acids was assumed by *Hehner* and *Mitchell*,[4] a specimen of oil examined by them having given 7 per cent of "stearic acid" crystals of the melting point 67° C. It is very likely that this "stearic" acid consisted chiefly of "arachidic" acid, of which arachis oil contains about 5 per cent.

Amongst the liquid fatty acids of arachis oil *Gössmann* and *Scheven*,[5] and also *Schröder*,[6] claim to have found the unsaturated fatty acid—hypogæic acid (Vol. I. Chap. III.). *Schoen*,[7] however, having been unable to detect this acid, asserts that oleic acid is the only unsaturated acid in arachis oil. *Hazura's*[8] conjecture that hypogæic acid forms a constituent of the unsaturated glycerides in arachis oil is confirmed by the fact that synthetical hypogæic acid has the same properties as the natural acid found in arachis oil by *Gössmann* and *Scheven*, and *Schröder* (cp. Vol. I. Chap. III.).

Amongst the liquid fatty acids of arachis oil *Hazura* and *Grüssner* identified linolic acid by means of its oxidation product, sativic acid. The amount of linolic acid from an arachis oil having the iodine value 82·9, was calculated by *Farnsteiner* from the isolated tetrabromide as about 6 per cent of the mixed fatty acids. Judging from the iodine value of the liquid fatty acids, as given in the table of characteristics of the insoluble fatty acids, this proportion appears much too low. In somewhat better agreement with the numbers given in the table is the statement, also due to *Farnsteiner*, that the insoluble fatty acids contain, besides oleic acid, 30·3 per cent of liquid fatty acids, of which linolic acid only forms a fraction. Since arachis oil contains no linolenic acid, the deficiency of unsaturated acids (to account for the high iodine value of the insoluble liquid fatty acids) may perhaps be explained, pending further investigation, by the assumption that hypogæic tetrabromide is soluble in petroleum ether.

[1] Wijs, *Zeit. f. Unters. Nahrungs- u. Genussm.* 1903, 492.
[2] *Liebig's Annalen*, 101. 97.
[3] *Berichte*, 21. 880.
[4] *Analyst*, 1896, 328.
[5] *Liebig's Annalen*, 94. 230.
[6] *Ibid.* 143. 22.
[7] *Ibid.* 244. 253; *Berichte*, 21. 878.
[8] *Monatshefte*, 10. 242.

Physical and Chemical Characteristics of Arachis Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9193	Valenta	− 2·5	Schoen	190·1-197	Dieterich	103	Hübl
,,	0·9173	Del Torre	0 to	Lewko-	189·3 [1]	Thomson and	87·3-90	Dieterich
,,	0·9171 [1]	Thomson and	+2	witsch		Ballantyne	96·7-98·7	Filsinger
		Ballantyne		Sadtler	191·1 [2]	,,	101·3	Del Torre
,,	0·9209 [2]	,,	+3 [8]	,,	192·7-194·6	Schoen	85·6-98·4	Schoen
,,	0·917 [2]	De Negri and Fabris	+3 [9]	,,	190·2 [2]	De Negri and	95-95·4 [3]	De Negri and
,,	0·9200 [3 4]	,,	+2 [10]			Fabris		Fabris
,,	0·9165 [5]	,,			193·1 [3]	,,	97·9-100 [4]	,,
,,	0·917 [8]	Sadtler			191·4-192 [4]	,,	92-92·7 [5]	,,
,,	0·9175 [9]	,,			189·4 [5]	,,	90·2	Lewkowitsch
,,	0·911 [10]	,,			185·6-194·8 [7]	Crossley and	101-105	Oliveri
15·5	0·9195	Crossley and				Le Sueur		
(water		Le Sueur			191-196	Oliveri	96·55-98·98	Schweitzer and
15·5 = 1)	0·9256 [7]	,,						Lungwitz
15·5	0·9186-0·9188	Tolman and Munson			194-196	Thoerner	94-96	Thoerner
,,	0·91795	Lewkowitsch					92·4-	Crossley and
20	0·9118-0·9125 [10]	Wijs					100·82 [7]	Le Sueur
,,	0·9139-0·9145 [8]	,,					83·3-84·1 [6]	Tortelli and
,,	0·9153 [11]	,,						Ruggeri
22	0·911-0·916	Schoen					84·6 [7]	,,
23	0·917-0·918	Dieterich					91·75 [8]	Sadtler
99	0·8673	Allen					94·17 [9]	,,
(water								
15·5 = 1)								

[1] Refined oil. [2] Commercial oil. [3] From Pondichéry nuts. [4] From Coromandel nuts.
[5] From Mozambique nuts. [6] From Rufisque nuts.
[7] East Indian oils ; the acid values of these oils, four in number, are recorded in the table p. 252.
[8] Virginian nuts, *Amer. Journ. Phar.* 1897, 69, 490-492. [9] Spanish nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492.
[10] African nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492. [11] Egyptian nuts.

Physical and Chemical Characteristics of Arachis Oil—continued

Reichert-Meissl Value.		Maumené Test.		Refractive Index.			Viscosity.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At °C.		Observer.	No. of Seconds At 70° F.	Observer.
0·0	Crossley and Le Sueur	56-75[10]	Sadtler	15	1·4731	Procter	350·1[8]	Crossley and Le Sueur
0·48[10]	Sadtler	58	Del Torre	15·5	1·4723	Tolman and Munson	347·0	,,
1·60[11]	,,	49[3]	De Negri and Fabris[9]	20	1·4698	Harvey	429·3	,,
		51[4]	,,	60	1·4545	Thoerner	306·9	,,
		46[5]	,,					
		45·5[2]	,,					
		49	Archbutt					
		Specific Temperature Reaction.		Oleo-refractometer.				
				"Degrees" at 22° C.		Observer.		
		105[1]	Thomson and Ballantyne	+3·5[6] to +6·5[7]		Jean		
		137[2]	,,	+4		Bruyn and van Leent		
				+5 to +7		Pearmain		
				Butyro-refractometer.				
				At °C.	"Degrees."	Observer.		
				15·5	70-71·3	Tolman and Munson		
				25	66·5	Beckurts and Seiler		
				,,	65·8-67·5	Mansfeld		
				40	57·5	Crossley and Le Sueur		

[1] Refined oil. [2] Commercial oil. [3] From Pondichéry nuts. [4] From Coromandel nuts. [5] From Mozambique nuts.
[6] From Rufisque nuts. [7] From Boulam nuts. [8] East Indian oils; the acid values of these oils, four in number, are recorded in the table p. 252.
[9] Jean's thermelæometer. [10] Virginian nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492. [11] Spanish nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·86	Bensemann	92·5	0·8436	Schoen	23·8	Hübl	27·7	Hübl	201·6	Thoerner	281·8	Allen	95·5-96·9	Morawski and Demski	1·4461	Thoerner
94·87 [10]	Sadtler	98·5	0·8468	,,	28	Allen	27·8-29·5	Allen					103·42 [2]	De Negri and Fabris		
95·31 [9]	,,	99 (water 15·5=1)	0·846	Allen	29-29·5	Dieterich	31·5-32	Dieterich					96·53 [4]	,,		
		100 (water 100=1)	0·8790	Archbutt	31	Bach	31-32 to 34-35	Bensemann [5]					96-97	Thoerner		
							33	Bach								
							30	Schoen								
					25-23 [1]	De Negri and Fabris	29-31 [1]	De Negri and Fabris					Iodine Value of the Liquid Fatty Acids.			
					25-22 [2]	,,	28-30 [2]	,,								
					24-22 [3]	,,	27-29 [3]	,,								
					25-23 [4]	,,	28-30 [4]	,,								
					29-30	Thoerner	30-32	Thoerner					128·5	Wallenstein and Finck		
					32·5 [9]	Sadtler	34 [9]	Sadtler					111·0-119·5	Lane		
					27·5 [10]	,,	29 [10]	,,					122·4-123·4 [6]	Tortelli and Ruggeri		
					Titer Test.								104·7-105·5 [7]	,,		
													106 [8]	,,		
					28·1-29·2 [4]	Lewkowitsch										

[1] From Pondichéry nuts. [2] From Coromandel nuts. [3] From Mozambique nuts. [4] Commercial oil. [5] Bensemann's method.
[6] Iodine value of oils : 92·2-93·5. [7] From Rufisque nuts ; iodine value of oil : 83·3-84·1. [8] From Gambia nuts ; iodine value of oil : 84·6.
[9] Spanish nuts. [10] Virginian nuts.

The true acetyl value of a sample of arachis oil examined in the author's laboratory—having the acid value 2·17—was 9·02 to 9·09. The "cold-drawn" oils only contain small amounts of free fatty acids; their amount is somewhat higher in the commercial oils intended for technical purposes. In the following table I collate a number of observations :—

No.	Description of Oil.	Number of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
			Per cent.	
1	Expressed, salad oil .	13	0·85 to 3·91	Nördlinger
2	Expressed, commercial oil	12	3·58 to 10·61	,,
3	Extracted oil . . .	16	0·95 to 8·85	,,
4	Refined oil . . .	1	0·62	Thomson and Ballantyne
5	Commercial oil . .	1	6·20	,,
6	Indian oil . . .	1	2·9	Crossley and Le Sueur
7	,, ,, . . .	1	4·8	,,
8	,, ,, . . .	1	16·5	,,
9	,, ,, . . .	1	13·1	,,

Oils No. 4 and No. 5 of the table contained 0·54 and 0·94 per cent of unsaponifiable matter respectively.

Samples No. 6, 7, 8, 9, examined in a Laurent polarimeter, showed in a 200-mm. tube the rotations $-0°7'$, $+0°24'$, $\pm 0°0'$, and $-0°7'$ respectively; the optical activity cannot, therefore, be caused by the glycerides themselves.

Arachis oil can be identified and detected with certainty by the isolation of "arachidic acid." The arachidic acid obtained by the following method is in truth a mixture of arachidic and lignoceric acids, and will be termed here "crude arachidic acid."

The method originally proposed by *Renard*[1] is carried out in the following manner :—Saponify 10 grms. of the oil, separate the fatty acids from the soap solution by hydrochloric acid, dissolve these in 90 per cent alcohol, and add a solution of lead acetate. I shorten the process by neutralising the excess of alkali with acetic acid, using phenolphthalein as an indicator, and precipitating with lead acetate without isolating the fatty acids.[2] Filter off the precipitated lead salts, and extract them with ether in a Soxhlet apparatus, thus separating the lead salts of the unsaturated acids from those of the saturated fatty acids (cp. Vol. I. Chap. VIII.). Decompose the latter with hydrochloric acid under ether; separate the ethereal layer of the fatty acids from the lead chloride which remains partly in solution, and distil off the ether. Next dissolve the residue in 50 c.c. of hot 90 per cent (by volume) alcohol. If arachis oil is present in the sample, a crop of crystals consisting of crude arachidic acid will be obtained on

[1] *Compt. rend.* 73. 1330.

[2] Kreis (*Journ. Soc. Chem. Ind.* 1895, 688) suggests the use of an *alcoholic* solution of lead acetate.

cooling the alcoholic solution. Filter the crystals off and wash on the filter, first with a measured quantity of 90 per cent, then with 70 per cent (by volume) alcohol, which dissolves but small quantities thereof, and finally dissolve them by pouring boiling absolute alcohol on the filter, receiving the filtrate in a porcelain dish or in a flask. Evaporate to dryness and weigh the residue. Add to the weight of crude arachidic acid thus found the quantity dissolved by the 90 per cent alcohol used for washing, taking as basis for calculation that 100 c.c. dissolve 0·022 grm. at 15° C., or 0·045 grm. at 20° C. Finally determine the melting point of the crude arachidic acid, which should be from 71° to 72° C. *Renard* isolated 4·5 to 5·0 per cent, *Allen* 5·5, and *De Negri* and *Fabris* 4·37 to 4·80 per cent of "arachidic acid" from samples of genuine arachis oil. Hence the amount of acid found will represent roughly $\frac{1}{20}$ of the arachis oil present, and the latter may therefore be approximately calculated by multiplying the weight of the crude arachidic acid by 20. *Bellier*[1] proposes the factor 23·81.

To test the accuracy of the method *De Negri* and *Fabris*[2] have examined prepared mixtures of olive oil and arachis oil and obtained the following numbers :—

Sample Containing		Crude Arachidic Acid Found.			Arachis Oil Found.
Olive Oil.	Arachis Oil.	Weighed as Crystals.	Calculated as Dissolved.	Total.	Per cent.
Per cent.	Per cent.	Grms	Grms.	Grms.	
70	30	0·107	0·0315	0·1385	29·08
80	20	0·0605	0·0315	0·0920	20·24
85	15	0·0385	0·0315	0·070	14·00
90	10	0·0200	0·0315	0·0515	10·30
90	10	traces			
90	10	0·0280	0·0154	0·0434	9·54
90	10	traces			

It will thus be seen that on employing 10 grms. of the sample, the limit is reached if it contain only 10 per cent of arachis oil. It will therefore be advisable to take from 20 to 40 grms. of the sample according to the quantity of arachis oil it may be suspected of containing, and to double or quadruple the proportions of 90 per cent alcohol required to dissolve the solid fatty acids.

Tortelli and *Ruggeri*,[3] in an exhaustive examination of *Renard's* method, found that the solubilities in 90 per cent alcohol, as given by *Renard*, are too low. Their method of isolating the crude arachidic acid (see below) leads to a mixture of acids melting between 74° C. and 75·5° C., for which the following solubilities have been ascertained :—

[1] *Ann. chim. anal. appl.* 1899 [4], 4.
[2] *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 123.
[3] *Journ. Soc. Chem. Ind.* 1898, 877.

100 *c.c. of* 90 *per cent Alcohol dissolve Crude Acid of M.P.* 74°-75·5° *C.*

Amount of Acid taken.	Of Melting Point.	Amount of Acid dissolved			The amount of Crude Acid employed corresponds to
		At 15° C.	17·5° C.	20° C.	
Grms.	° C.	Grms.	Grms.	Grms.	
2·7000	74·3-74·5	0·0729	0·0820	0·0910	}
1·5600	75·1-75·5	0·0715	0·0801	0·0922	} More than 20 grms. of arachis oil
1·2506	74·8-75·5	0·0730	0·0811	0·0902	}
1·0000	74·3-74·5	0·0688	0·0866	0·0914	}
0·9604	74·0-74·6	0·0680	0·0869	0·0918	} About 20 grms. of arachis oil
0·5503	74·0-74·6	0·0650	0·0806	0·0879	} Mixtures containing about 50 per
0·5008	74·0-74·6	0·0643	0·0799	0·0844	} cent of arachis oil
0·3899	74·4-75·5	0·0602	0·0673	0·0740	} Mixtures containing 40 per cent of arachis oil
0·2615	74-75	0·0539	0·0610	0·0680	} Mixtures containing 27 per cent of arachis oil
0·1690	74-75	0·0447	0·0544	0·0662	} Mixtures containing 18 per cent of arachis oil
0·1064	74-75	0·0343	0·0402	0·0472	} Mixtures containing 11 per cent of arachis oil
0·0504	74·7-75·5	0·0301	0·0398	...	} Mixtures containing 5 per cent
0·0505	74·2-74·6	0·0314	0·0410	...	} of arachis oil

For practical purposes these numbers may be condensed as follows :—

100 *c.c. of* 90 *per cent Alcohol dissolve Crude Acid of M.P.* 74°-75·5° *C.*

For Amount of Acid.	At 15° C.	17·5° C.	20° C.
From 2·7 down to 0·5 grms.	0·070	0·080	0·090
,, 0·47 ,, 0·17 ,,	0·050	0·060	0·070
,, 0·11 ,, 0·05 ,,	0·033	0·040	0·045

In order to obtain crude arachidic acid of a melting point 74°-75·5° C. *Tortelli* and *Ruggeri* modify the *Renard* test in the following manner :— The lead salts of the solid fatty acids are prepared from 20 grms. of oil as described above, and the liberated solid acids are dissolved in 100 c.c. of 90 per cent alcohol by warming on the water-bath to about 60° C. If a slight turbidity be noticeable, one drop of very dilute hydrochloric acid may be added. Then allow to stand for three hours at a temperature of 15° to 20° C. The acid which separates out on cooling is thrown on a filter, the filtered alcoholic solution being used to transfer the crystals completely on to the filter. The crystals are washed three times each with 10 c.c. of 90 per cent alcohol, and then several times with 70 per cent alcohol.

The crystals on the filter are next dissolved in boiling absolute alcohol, the solution being received in a flask. The absolute alcohol is distilled off, the residue dissolved in 100 c.c. of 90 per cent alcohol as already described, and the crystals washed on a filter with 90 per cent and 70 per cent alcohol exactly as before. The washing with 70 per cent alcohol is discontinued when the wash-alcohol no longer dissolves appreciable quantities. Finally the crystals are dissolved in absolute alcohol, and their weight is determined.

The crystals should then melt between 74° and 75·5° C. On observing the alcoholic solution of the solid fatty acids when taken from the water-bath to cool, it will be readily noticed that the crystals represent a mixture of arachidic and lignoceric acids. At first very fine, lustrous needles separate in tufts—lignoceric acid; afterwards there appear larger quantities of very thin, shining laminæ of nacreous lustre—arachidic acid. The separation commences in the case of pure arachis oil at about 35° to 38° C., the temperature of crystallisation falling as the proportion of arachis oil in a given sample decreases (cp. table, p. 256). The following table gives the amounts of "arachidic acid" found in some arachis oils by *Tortelli* and *Ruggeri*:—

Crude Arachidic Acid found in Arachis Oils

Source of Oil.	Crude Acid.	
	Per cent.	Melting Point. °C.
Buenos Ayres, expressed at 45° to 50° C.	5·24	74·4-74·7
,, extracted with ether	4·92	74·2-74·8
Rufisque, first expression	4·31	74·2-74·6
,, second expression	4·55	74·4-75·2
Gambia, first expression	4·59	74·5-75·1
Commercial, French	5·33	74·1-74·4
,, Spanish	5·40	74·3-75·4

For practical purposes, when the amount of arachis oil in admixture with other oils has to be determined, it will be near enough to take 4·8 per cent as the mean proportion of crude arachidic acid, melting point 74°-75·5° C. in commercial arachis oils.

The following table may serve as a corollary to the one given by *De Negri* and *Fabris*; the numbers are due to *Tortelli* and *Ruggeri*:—

[TABLE

Sample containing		Temperature at which crystals separate from 90 per cent Alcohol.		Crude Arachidic Acid found.				M.P. of Crystals.	Arachis Oil found.
				Weighed as Crystals.	Dissolved (calculated).	Total.			
Olive Oil.	Arachis Oil.		90 per cent Alcohol used.						
Per cent.	Per cent.	° C.	c.c.	Grms.	Grms.	Grms.	Per cent.	° C.	Per cent (approx.)
0	100	37·7	260 at 15° C.	0·8894	0·1768	1·0662	5·33	74·1-74·3	100
40	60	31·8	150 ,, 17·5	0·5231	0·1200	0·6431	3·22	74-74·6	60
50	50	29·0	250 ,, 75	0·3931	0·1500	0·5431	2·72	74-74·6	50
60	40	25·5	280 ,, 75	0·2770	0·1509	0·4279	2·14	74·5-75·1	40
70	30	23·2	260 ,, 75	0·2056	0·1300	0·3356	1·68	74·1-74·6	31
80	20	21·0	250 ,, 75	0·1260	0·1150	0·2410	1·21	73·9-74·4	22
90	10	18·8	220 ,, 15	0·0514	0·0682	0·1196	0·60	72·2-74·6	11
95	5	16·7	150 ,, 15	0·0241	0·0434	0·0675	0·34	73-73·5	6·7

Archbutt[1] confirms the numbers given by *Tortelli* and *Ruggeri* for the solubilities of crude arachidic acid, and computes the following corrections :—

Correction per 100 *c.c. of* 90 *per cent Alcohol used for Crystallisation and Washing*

For Weights of Fatty Acids obtained by Renard's Process.	Grms. at		
	15° C.	17·5° C.	20° C.
0·1 or less . .	+0·033	+0·039	+0·046
0·2 ,, . .	0·048	0·056	0·064
0·3 ,, . .	0·055	0·064	0·074
0·4 ,, . .	0·061	0·070	0·080
0·5 ,, . .	0·064	0·075	0·085
0·6 ,, . .	0·067	0·077	0·088
0·7 ,, . .	0·069	0·079	0·090
0·8 ,, . .	0·070	0·080	0·091
0·9 and upwards .	0·071	0·081	0·091

Archbutt considers it unnecessary to convert the total fatty acids into lead salts ; he therefore recommends the following modification of *Renard's* process :—Dissolve the fatty acids obtained from 10 grms. of oil [by decomposing the saponified mass with hydrochloric acid under ether and evaporating off the solvent] in 50 c.c. of 90 per cent alcohol ; add to the solution, which must not be allowed to cool below 38° (to prevent separation of crystals), 5 c.c. of a 20 per cent aqueous solution of lead acetate, cool to about 15° C., agitate, allow to stand for half an hour, filter and wash once with ether. Return the soaps into the flask with the help of ether, digest with ether, and repeat this operation three times ; the lead oleate will thus be entirely dissolved out. Transfer the solid soap with the help of ether into a separating funnel, decompose with hydrochloric acid and wash the ethereal layer

[1] *Journ. Soc. Chem. Ind.* 1898, 1124.

free from mineral acid. Distil off the ether, dry the fatty acids in the hot-water oven, and pour into the flask 50 c.c. of alcohol of exactly 90 per cent (spec. grav. 0·8340). Dissolve the fatty acids by warming the (corked) flask, and then allow to cool to either 15° C. or 20° C. Collect the crystals on a small filter, or better on a *Gooch* crucible, and wash three times with 10 c.c. of 90 per cent alcohol, each time at the same fixed temperature. The filtrate and washings are measured; the necessary corrections are found in the table given above.

The crystals are thoroughly washed with 70 per cent alcohol, in which the crude arachidic acid is quite insoluble, until the washings remain clear on adding water. It is not necessary, although advisable, to redissolve the acids in 50 c.c. of 90 per cent alcohol and repeat the operations just described. The crystals are dissolved in boiling ether and weighed after drying at 100° C. The correction is then added to the weight. The melting point of the mixed arachidic and lignoceric acids so isolated varied (by capillary tube method) from 71° to 72·5° C.; but even when working in exact accordance with *Tortelli* and *Ruggeri's* directions the melting point 74°-75° C. could not be obtained by *Archbutt*, his highest figure being 73·3° C. [It may be added that after recrystallising the acids repeatedly from 90 per cent alcohol the melting point was raised to 79·6° C.]

The following table shows in greater completeness the results obtained by *Archbutt* with one and the same sample of arachis oil:—

[TABLE

Estimations of Arachidic and Lignoceric Acids by different Methods in the same Sample of Arachis Oil

Weight of Oil taken.	Method.	Volume of Alcohol. / Temperature, °C. / Solubility Coefficient.	Arachidic and Lignoceric Acids.				
			Dissolved in the Alcohol.	Weighed.	Total.	Per cent.	Melting Point by Capillary Tube Method.
Grms.							°C.
10	Renard's; 2 grms. PbA_2 aq.; not recrystallised.	70 c.c. / 20° / 0·082	0·0574	0·4283	0·4857	4·86	71
10	Renard's; 4 grms. PbA_2 aq.; not recrystallised.	70 c.c. / 20° / 0·082	0·0574	0·4258	0·4832	4·83	71
10	Renard's; 1 grm. PbA_2 aq.; not recrystallised.	80 c.c. / 15° / 0·0625	0·0500	0·4480	0·4980	4·98	71
10	Renard's; 2 grms. PbA_2 aq.; not recrystallised.	90 c.c. / 15° / 0·063.	0·0567	0·4554	0·5121	5·12	70
10	Renard's; 1 grm. PbA_2 aq.; recrystallised	130 c.c. / 15° / 0·061	0·0793	0·3931	0·4724	4·72	71
10	Renard's; 1 grm. PbA_2 aq.; recrystallised	135 c.c. / 15° / 0·061	0·0823	0·4125	0·4948	4·95	72
20	Tortelli's; exactly as described in *Chem. Zeit.* 1898, 600	265 c.c. / 17·5° / 0·079	0·2094	0·6935	0·9029	4·51	72
20	Renard's; 2 grms PbA_2 aq.; recrystallised; Gooch filter used . . .	250 c.c. / 15° / 0·070	0·1750	0·7649	0·9399	4·70	72·5
20	Renard's; 2 grms. PbA_2 aq.; recrystallised; Gooch filter used . . .	240 c.c. / 15° / 0·070	0·1680	0·7718	0·9398	4·70	72 72·8-72·3 (Bensemann)
20	Tortelli's; exactly as described; Gooch filter used	248 c.c. / 15° / 0·069	0·1711	0·6967	0·8678	4·34	72 72·3-73·3 (Bensemann)

This table may be supplemented by the following one showing the accuracy attainable in a practical case.

Results of Analysis of Mixtures of Olive Oil and Arachis Oil

Composition of Oil taken.		Volume of 90 per cent Alcohol. — Temperature. — Solubility Coefficient.	Arachidic and Lignoceric Acids.					Arachis Oil found.
Olive Oil.	Arachis Oil.		Dissolved in the Alcohol.	Weighed.	Total.	Per cent.	Melting Point.	
Per cent.	Per cent.						°C.	Per cent.
...	100	80 c.c. 15° 0·0625	0·0500	0·4480	0·4980	4·98	71	...
90	10	73 c.c. 15° 0·033	0·0241	0·0265	0·0506	0·506	71	10·2
80	20	73 c.c. 15° 0·033	0·0241	0·0715	0·0956	0·956	71	19·2

Tortelli and *Ruggeri*[1] maintain, however, that their modification is less cumbersome and leads to more correct results than the one suggested by *Archbutt*.

For *Tolman's* modification of *Renard's* test when applied to solid fats containing cotton seed oil the reader must be referred to the original paper.[2]

The determination of the crude arachidic acid is of the greatest importance in the examination of olive oils suspected of being adulterated with arachis oil, for the latter so closely resembles olive oil that judiciously prepared mixtures cannot be detected with certainty by means of the quantitative reactions. For although, as a rule, arachis oil has a higher iodine value than olive oil, a comparison of the numbers given in the table of characteristics for arachis and olive oils will show that there are in commerce arachis oils the iodine values of which approach closely those of olive oils having exceptionally high iodine values. The quantity of arachin naturally occurring in olive oil is too small to invalidate the correctness of the method. Nor would an admixture of rape oil seriously interfere with the information furnished by *Renard's* test, as special experiments, made in the author's laboratory, have shown. These experiments have been confirmed by *Archbutt's* determination of the arachidic acid in rape oil (see also below p. 293, under "Olive Oil").

Adulterants of arachis oil are poppy seed, sesamé, cotton seed, and rape oils.

Poppy seed oil is indicated by a high iodine value and specific gravity of the sample.

[1] *Moniteur Scientif.* 1902 [4], 215; cp. also Perrin, *Moniteur Scientif.* 1901 [4], 320.

[2] Cp. W. B. Smith, *Journ. Amer. Chem. Soc.* 1907 [29], 1756.

Sesamé oil is recognised by the furfural reaction. It has been pointed out above that a very faint *Baudouin* colour reaction need not necessarily indicate adulteration. In doubtful cases it is advisable to determine the iodine value of the oil, as also of its liquid fatty acids, and the solidifying point of the insoluble fatty acids.

Cotton seed oil is detected by the same quantitative reactions; the colour reactions described above (p. 162) will serve as confirmatory tests.

Rape oil would be revealed by a lower saponification value of the oil than the normal one, and by low solidifying and melting points of the mixed fatty acids.

Very large quantities of arachis oil are expressed in the south of France; considerable quantities are also prepared in Valencia (Spain), in Trieste, and in Holland. In this country as yet no arachis oil is made. It has been pointed out already that the oils of first expression are used as salad oils. They are largely employed for adulterating, or even wholly substituting, olive oils, also for blending with olive oil; thus the Valencia oil is specially known to be mixed with Andalusian olive oil, in order to neutralise the harsh flavour of the latter. Edible arachis oil is further used for preserving sardines. The oils of second and third expression are chiefly used in soap-making. One of the characteristic components of the Marseilles white soap is arachis oil.

RICE OIL[1]

French—*Huile de riz.* German—*Reisöl.* Italian—*Olio di riso.*

For tables of characteristics see p. 261.

This oil, as obtained in this country from Rangoon rice meal (from *Oryza sativa*, L.) by hydraulic pressure, has a dirty greenish colour. Rangoon rice meal contains about 15 per cent of oil, common rice meal only 8-9 per cent.

The oil obtained from fresh rice bran is practically neutral, but, on standing, the proportion of free fatty acids very rapidly increases owing to the action of an enzyme, as has been shown by *Browne.*[2] Thus the oil examined by *Smetham* contained from 31·6 to 72·2 per cent, and the specimen examined by *Browne* 83 per cent of free fatty acids. This fact explains the high melting point of a commercial oil, viz. 24° C., observed by *Browne.* *Twitchell* found in a specimen of rice oil 4·37 per cent of unsaponifiable matter (chiefly phytosterol). This specimen of oil contained 46·2 per cent of free fatty acids.

The occurrence of an enzyme in rice bran was demonstrated by *Browne*, by mixing 20 c.c. of a 20 per cent cold aqueous extract of rice bran with an equal volume of castor oil. After twenty-four

[1] Smetham, *Journ. Soc. Chem. Ind.* 1893, 848.
[2] *Journ. Soc. Chem. Ind.* 1903, 1137.

hours the emulsion became acid, and after one week the proportion of free fatty acids had risen to 16 per cent. It appears to me not unlikely that the action of the lipase had been arrested in this experiment, since *Browne* had rendered the mixture faintly alkaline to litmus. Further proof of the view that the production of free fatty acids is due to an enzyme is given by an experiment, in which freshly ground rice bran was divided into two portions, one of which was heated to 100° C. to destroy the enzyme. After one month the oil was extracted from both samples. The results of this experiment are reproduced in the following table :—

	Free Acid as Oleic Acid. Per cent.
Raw rice (stored many months) . .	6·9
Fresh bran (six hours after grinding) . .	12·5
Bran, one month old, unheated . .	62·2
,, ,, heated . . .	24·0

Rice oil is now prepared in considerable quantities in Louisiana, by extracting the bran with solvents, and an outlet for the oil is being sought in the soap industry.[1]

Physical and Chemical Characteristics of Rice Oil

Specific Gravity.		Solidifying Point. °C.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Maumené Test. °C.	Refractive Index.	Observer.
At °C.			Mgrms. KOH.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.		Butyro-refractometer. "Degrees." At 25° C.	
99	0·8907		193·2		96·4			Smetham
(water 99=1)			193·5	1·1	91·65			Browne
15	0·923	2·1			106·5	66·7	68·2	Fabris[2] and Settimj

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Observer.	Iodine Value.	
					Per cent.	Observer.
		36	289·3	Browne	97·4	Twitchell[3]
95·6	28-29	31-32		F. and S.	109	F. and S.[4]

[1] Cp. "Rice Oil Industry, Louisiana," *Zeit. f. ang. Chem.* 1905, 1239.

[2] The oil was extracted from Italian rice germs, and gave 30 per cent of solid and 70 per cent of liquid fatty acids.

[3] Private communication.

[4] Iodine value of liquid fatty acids 130·7.

TEA SEED OIL

French—*Huile de thé ; huile de camellia.* German—*Theesamenöl.* Italian—*Olio di thè.*

For tables of characteristics see p. 263.

Tea seed oil is obtained from the seeds of *Thea sasanqua*[1] (Thunb.), Nois, which is specially cultivated in China, Tonkin, and Assam for its fruits and not for its leaves. The oil is expressed on a large scale in China ; the first pressed oil serves there as an edible oil,[2] although the proportion of saponin it is said to contain would render it somewhat unsafe for consumption. The oil obtained by extraction with solvents is perfectly free from saponin ;[3] the lower qualities are used as burning oil and for soap-making. There are two varieties, viz. Chinese and Assam oil. Chinese tea seed yields 30-35 per cent, Assam tea seed 43-45 per cent of oil.

Tea seed oil is straw or amber coloured, closely resembling olive oil ; like the latter it gives a hard elaïdin. The proportion of liquid fatty acids determined by the lead-salt-ether method was found by *Lane* in two samples of tea seed oil to be 88 per cent and 93·2 per cent respectively.

The fatty oil from *Camellia oleifera*, Bot. Reg., a plant largely cultivated in China for the sake of the pale bland oil prepared from its seeds—"Cha-yow oil"—is not used for edible purposes, but as a hair oil or a burning oil. Its specific gravity is 0·9175 at 15° C.

The foregoing gives a *résumé* of the notes published in the literature on tea seed oil ; but as the statements regarding the origin of the oils examined by the various observers are extremely indefinite, all the numbers must be accepted with reserve. To a great extent they may be considered as superseded by the description of the following two oils—"Tsubaki Oil" and "Sasanqua Oil." According to the system adopted in this work the following two oils should be placed further below, having regard to their iodine values ; they are described here on account of their near relationship to the commercial tea seed oils examined hitherto.

The seeds of the ordinary tea plant (*Thea sinensis*, L.) contain a fatty oil, but since in the cultivation of tea leaves the development of the seed is mostly suppressed, the oil has no commercial importance.[4]

[1] Synonyms are : *Camellia drupifera*, Lour. ; *Thea oleosa*, Lour. ; *Thea drupifera*, Pierre ; *Camellia oleifera*, Wall. A specimen of oil from *Camellia drupifera*, Lour., originating from Cochin China, was examined by Pottier (*Les Nouveaux Remèdes*, 1900, 16, 121), and is stated to have the specific gravity 0·980 (!), and to rotate the plane of polarised light 1·8° to the right in a 200-mm. tube.

[2] The Jesuit D'Incarville, about 1735, mentions already the use of this oil for edible purposes in China.

[3] Weil, *Arch. d. Pharm.* 239, 365.

[4] For a description of the oil see Appendix.

Physical and Chemical Characteristics of Tea Seed Oil

	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Refractive Index. Oleo-refractometer.	
	At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	"Degrees."	Observer.
Chinese oil	15	0·917-0·927	Schaedler	− 5	Schaedler	195·5	Davies	88	Itallie	+ 8	Pearmain
Assam oil	15	0·920	Itallie [1]	− 12	Itallie	194	Itallie	90·49	Lane	at 22° C.	
Japanese oil	20	0·9110	Wijs [2]			188·3	Wijs	88·9	Wijs		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
91·5	Itallie	10-11	Wijs	195	Wijs	287·6	Wijs	90·8	Wijs
								Liquid Fatty Acids.	
								99·6-104·4 [3]	Lane

[1] *Journ. Soc. Chem. Ind.* 1894, 79. [2] *Zeit. f. Unters. Nahrungs- und Genussm.* 1903, 492. [3] Calculated.

TSUBAKI OIL [1]

French—*Huile de tsubaki.* German—*Tsubakiöl.*
Italian—*Olio di tsubaki.*

This oil is obtained from the seeds of *Thea japonica*, Nois (*Camellia japonica*, L.). The tsubaki tree is planted in Japan for ornamental purposes on account of its beautiful flowers. In certain parts of Japan it grows wild in such abundance that the seeds are worked for the preparation of oil, as in the islands of Idzu, in the Shidzuoka prefecture and several prefectures of Kiushiu (Kumamoto, Nagasaki, Oita). The fruit ripens in autumn, and the seeds fall to the ground. The seed is 2·25 cm. long; its weight varies from 1·2 to 3 grams. A specimen from Oshima examined by *Tsujimoto* consisted of 41·5 per cent of husks and 58·5 per cent of kernels. Kernels from different localities gave the following results:—Moisture, 4·24-4·93 per cent; oil, 64·3-66·4 per cent; ash, 1·6-1·75 per cent.

The seeds are dried by exposure to sunlight, crushed, steamed, and pressed twice in the Japanese wooden wedge press ("tatsugi") usually employed in Japan. Other manufacturers decorticate the seeds previous to crushing. The process in which the whole seeds are crushed yields 15 per cent of oil (by volume).

The oil prepared from fresh seeds by pressing is pale yellow and practically odourless. Its taste is mild and pleasant.

Commercial tsubaki oil has a yellow colour, and a slight peculiar odour; the inferior, decidedly rancid grades vary from yellow to reddish yellow. The following characteristics are given:—

	Cold-drawn Oil.	Commercial Oil.	Oil from Decorticated Seed.
Oil—			
Specific gravity at 15·5° C.	0·9159-0·9163	0·9161-0·9166	0·9160
Saponification value	190·6-192·6	180·9-190·6	191·9
Iodine value	80·3-81·3	80·1-80·6	80·4
Reichert-Meissl	0·5		
Refractive index at 20°	1·4682-1·4691	1·4691-1·4679	1·4687
Fatty Acids—			
Insoluble acids + unsaponifiable	95·5%		
Specific gravity at 100° C. (water at 15° = 1)	0·8402		
Melting point	22° C.		
Neutralisation value	197		
Mean molecular weight	284		
Iodine value	83·7		

The oil solidifies completely at −15° C. In Valenta's test it becomes rancid at 81° C. In the elaidin test the oil solidifies in two hours; after twenty-four hours a very hard mass is obtained.

[1] Tsujimoto, *Journ. Coll. Engin. Imp. Univ. Tokyo, Japan*, 1908. vol. iv. p. 75.

The acid values of a number of cold-drawn oils described above varied from 1·63 to 2·67; the commercial samples had higher acid values, rising up to 8·8.

The mixed fatty acids were separated by the lead-salt-ether method into 93·1 per cent of liquid fatty acids of the iodine value 89. They seem to consist of oleic acid; for on bromination no ether-insoluble compounds were obtained, nor could sativic acid be detected among the oxidation products of the acids (*Kametaka*).

Tsubaki oil is the highest priced of all Japanese vegetable oils, and is therefore largely adulterated with rape, cotton seed, soja bean, and arachis oils. *Tsujimoto* finds *Bieber's* reagent suitable for the detection of all these adulterants; but in view of the characteristic quantitative reactions which can be applied with greater certainty, the table of colour reactions given by *Tsujimoto* is not reproduced here.

Tsubaki oil is chiefly used as a hair oil. In the islands of Idzu it is used as an edible oil. Owing to its high price its industrial use is limited. It is sometimes used as a lubricating oil for delicate machinery.

SASANQUA OIL [1]

French—*Huile de sasanqua.* German—*Sasanquaöl.*
Italian—*Olio di sasanqua.*

This oil is prepared from the seeds of *Thea sasanqua*, Nois (*Camellia sasanqua*, Thun [2]), a tree which is very similar to the tsubaki tree, and is used like the latter for ornamental purposes. The sasanqua seeds resemble those of tsubaki but are smaller, their length varying from 1·0 to 1·5 cm.; their weight is on the average 0·5 grams. The seeds consist of 28 per cent of husk, and 72 per cent of kernels. An analysis of the kernels gave the following result:—Moisture, 5·11-5·78 per cent; oil, 58·1-59·4 per cent; ash, 1·7-1·8 per cent.

The oil is prepared commercially in the prefecture Kumamoto by drying the seeds, powdering, steaming, and finally pressing in a wooden wedge-press. The mass is generally expressed twice, so that 16 to 17 per cent of oil (by volume) are obtained thereby.

The examination of a cold-pressed oil (from Amakusa seed) and an oil extracted with ether (from Tokyo seed) gave the following results:—

[1] Tsujimoto, *Journ. Coll. Engin. Imp. Univ. Tokyo, Japan*, 1908, vol. iv. p. 80.

[2] A plant named *Camellia oleifera*, grown in China, appears to be of the same species as sasanqua.

	Cold-pressed Oil.	Extracted Oil.
Oil—		
Specific gravity at 15° C.	0·9163	0·9188
Saponification value	193·9	193·4
Iodine value	82·3	81·7
Reichert-Meissl value	1·17	
Refractive index at 20° C.	1·4691	1·4961[1]
Fatty Acids—		
Specific gravity at 100° C. (water at 15·5 = 1)	0·8405	
Melting point	28° C.	
Neutralisation value	199·64	
Mean molecular weight	281	
Iodine value	86·1	

The samples examined had the acid values 6·78 and 0·4 respectively. The oil solidifies completely at − 9° C. In the elaïdin test it solidifies in two hours to a hard mass.

The fatty acids treated by the lead-salt-ether method yielded 89·9 per cent of unsaturated acids (of the iodine value 92·9). No insoluble bromide was obtained on treating the acids with bromine. The chief constituent of sasanqua oil is, therefore, oleine.

Sasanqua oil resembles tsubaki oil very closely. *Tsujimoto* is of the opinion that with the aid of *Bieber's* reagent this oil can be distinguished from tsubaki oil.

Sasanqua oil is chiefly used as a hair oil (as a substitute (?) for tsubaki oil). It is also employed as a lubricating oil.

NJORE-NJOLE OIL[2]

The fruits of the "Ossidinge" tree, growing profusely in the wild state in the Cameroons (West Africa), enclose two or three kernels of the size of an almond. The kernels, known to the natives as "Njore-Njole," weigh 1·2 to 1·4 grams, and contain 62 per cent of an oil, the bulk of which can be expressed in the cold. The oil so obtained has a pleasant taste.

The following characteristics were ascertained :—

Specific gravity (at 15° C. ?)	0·9135
Solidifying point	− 1 to − 1·5° C.
Saponification value	193·1
Iodine value	93·4
Refractive index at 22° C.	1·4695

[1] It would appear that this figure should also be 1·4691.

[2] Brieger and Krause, *Der Tropenpflanzer*, xii. No. 2.

INOY KERNEL OIL

The inoy kernel oil is obtained from the seeds of *Poga oleosa*, Pierre, a plant indigenous to West Africa.[1] The seeds yield on extraction with petroleum spirit 60·8 per cent of oil. The examination of the oil[2] gave the following numbers:—

Iodine value	89·75
Reichert-Meissl value	1·45
Insoluble fatty acids + unsaponifiable	93 per cent.
Titer test of the fatty acids	22° C.
Acid value of the specimen	5·2

The specimen which the author obtained from the Imperial Institute deposited a "stearine" on keeping.

PISTACHIO OIL[3]

French—*Huile de pistache.* German—*Pistazienöl.*
Italian—*Olio di pistacchio.*

This oil is contained in the seeds of the pistachio nuts (from *Pistacia vera* or *P. lentiscus*, L.). Oil obtained by extraction with ether has a more pronounced aromatic odour than that expressed in the cold.

Pistachio oil has a very limited commercial application; it is used in the manufacture of sweetmeats.

Physical and Chemical Characteristics of Pistachio Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Maumené Test.	Butyro-refractometer. "Degrees."
At 15° C.	° C.	Mgrms. KOH.	Per cent.	° C.	At 25° C.
0·9185	−8 to −10	191·0-191·6	86·8-87·8[4]	44·5-45[4]	62[4]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Iodine Value.
Per cent.	° C.	° C.	Per cent.
96·1[4]	13 14-13	17-18 18-20	88·9 96·2[4]

[1] Cp. Pierre, *Bull. Soc. Linn. Par.* 1896, ii. 1254. Pierre places the plant in the natural order *Phytolaccaceæ*; it is known to the natives as M'poga.

[2] *Bulletin of the Imperial Institute*, 1906, p. 201; cp. also Edie, *Quar. Journ. Inst. of Comm. Research in the Tropics*, 1907, 14.

[3] De Negri and Fabris, *Annali del Lab. Chim. delle Gabelle*, 1893, 220.

[4] Fabris and Settimj. These observers give the iodine value 92·5 and Maumené test 55° C. for an oil obtained by expression of Sicilian seeds. The oil yielded 80 per cent of liquid fatty acids of the iodine value 105·8.

HAZELNUT OIL

French—*Huile de noisette.* German—*Haselnussöl.*
Italian—*Olio di nocciuole.*

For tables of characteristics see p. 269.

Hazelnut oil is prepared from the seeds of the hazelnut tree, *Corylus avellana*, L., by pressing or by extracting with solvents. The seeds contain from 50 to 60 per cent of oil.

This oil has a golden-yellow colour; it is transparent, and has the odour of hazelnuts. For want of better methods this characteristic odour must be used for its detection in other oils.

According to *Hanus*,[1] hazelnut oil consists of 85 per cent of oleic acid, 9 per cent of palmitic acid, and 1 per cent of stearic acid. The iodine value of the liquid acids as found by *Tortelli* and *Ruggeri* points, however, to the occurrence of linolic acid in hazelnut oil. *Fabris* and *Settimj*[4] found 80 per cent of liquid fatty acids in a specimen from dry hazelnuts which yielded 35 per cent of oil. In the elaïdin test hazelnut oil yields a solid white mass.

The specimen examined by *Hanus* contained 0·5 per cent of unsaponifiable matter, which was identified as phytosterol. The acetyl value was 3·2.

Hazelnut oil much resembles almond oil; the lower iodine value and the lower solidifying point may serve as means to distinguish the two oils.

Hazelnut oil is used in perfumery, and as lubricating oil for watch springs and other delicate machinery. According to *Filsinger*[2] it is also used in the adulteration of chocolate fats. *Bennett*[3] states that hazelnut oil is being substituted for peach kernel oil. Hazelnut oil, in its turn, is liable to adulteration with olive oil; the latter would be detected by a high solidifying point of the sample.

[1] *Chem. Ztg.* 1899, Ref. 226. [2] *Journ. Soc. Chem. Ind.* 1893, 5.
[3] *Chemist and Druggist*, 1908, 89.
[4] *Atti del VI. Cong. intern. di Chim. applic.*, Roma, 1907, vol. v. 755.

Physical and Chemical Characteristics of Hazelnut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Butyro-refractometer. "Degrees."	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At 25° C.	Observer.
0·9170	Massie	−20	Girard	197·1	Filsinger	88	Girard	0·99	Schoettler	35-36	De Negri and Fabris	61·2	F. and S.
0·9146	Filsinger	−10	Braconnot	192·8	De Negri and Fabris	88·5	Filsinger	0·99	Hanus	36·2	Hanus		
0·9170	De Negri and Fabris			191·4	Soltsien	86·2-86·8	De Negri and Fabris						
0·9164	Soltsien			187	Schoettler	83·2	Soltsien						
0·916	Schoettler			193·7	Hanus	87	Schoettler						
0·9169	Hanus					90·2	Hanus						
0·9155	Fabris and Settimj	−18	F. and S.			83·9	Tortelli and Ruggeri						

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
95·5	Schoettler	9	Soltsien	17	Soltsien	200·6	Hanus	90·1	De Negri and Fabris
				25	Girard			90·6	Hanus
95·6	Hanus	19-20	Schoettler	22-24	De Negri and Fabris			87·5	F. and S.
				24-25	F. and S.				
								Iodine Value of the Liquid Fatty Acids.	
								91·3	Hanus
								97·6	Tortelli and Ruggeri
								98·8	F. and S.

KOËME OIL [1]

French—*Huile de Telfairia ; huile de noix d'Inhambane.*
German—*Koëmeöl, Thalerkürbisöl (Telfairiaöl).*[2]
Italian—*Olio di telfairia ; olio di noce di Chilimanjaro.*

For tables of characteristics see p. 271.

This oil is obtained from the seeds of *Telfairia pedata*, Hook. fil. ; syn. *Joliffia africana*,[3] a tall climbing plant belonging to the *Cucurbitaceæ*. It is indigenous to the coast of South-East Africa and the islands off the East African Coast. The fruit reaches a length of 2 to 3 feet and a breadth of 8 to 10 inches. The fruits have internally three to six cells, each *loculus* containing a number of large, flat, almost circular seeds about $1\frac{1}{2}$ inches in diameter. The seeds are known in commerce as "Koëme de Zanzibar," "Kilima-Njaro nuts," [4] and are largely used as an article of food by the natives. The kernels have a pleasant taste, and do not easily become rancid even after keeping for several years, the shells apparently forming a good protection against the influence of the atmosphere. The sample examined by the author yielded 60·5 per cent of oil. A sample of seeds examined by *Bontoux* [5] gave 46 per cent of shells and 54 per cent of kernels. The kernels yielded, by extraction with carbon bisulphide, 62·57 per cent of oil, or calculated to the entire seeds 33·8 per cent. By expression of the kernels on a laboratory scale *Bontoux* obtained 50 per cent of oil.

Both kinds of oil extracted by *Bontoux* have a yellowish-red colour.

According to *Drabble* [6] the unshelled seeds contain 33-36 per cent of oil, the shelled seed yield 59 per cent.

The expressed oil has a pleasant and even sweet taste. Attempts to prepare an edible oil have hitherto failed owing to the difficulty of shelling the seeds by a cheap process. The removal of the shell must be carried out completely, as it has an extremely bitter taste, and may even give up toxic substances to the oil if expressed together with the pulp of the fruit (*Bontoux*).

The sample examined by the author had the acid value 0·56, and contained 0·9 per cent of unsaponifiable matter.

The oil gives the elaïdin reaction ; on exposure to the atmosphere for several months it becomes slightly viscous.

The mixed fatty acids contain stearic, palmitic, and telfairic (Vol. I. Chap. III.) acids, and possibly an unsaturated hydroxylated acid of the composition $C_{24}H_{40}O_3$. The acetyl value of the oil, viz.

[1] Thoms, *Arch. d. Pharm.* 238 (1900), 48. [2] Cp. *Jahrb. der Chemie*, ix. 354.
[3] This name is used for both *Telfairia pedata* and *T. occidentalis* ; the name *Joliffia africana* was first applied to *T. occidentalis*.
[4] Romagnoli, *L' industria saponiera*, iii. No. 3. [5] Unpublished observations.
[6] *Quarterly Journal of the Institute of Comm. Research in the Tropics*, vol. ii. No. 5 (1907), p. 135.

26·9, found by *Thoms*, is due to the presence of the hydroxylated acid. The remarkably low saponification value given by *Thoms* has not been confirmed by *Lewkowitsch* nor by *Bontoux*.

The seeds from *Telfairia occidentalis*[1] from the West Coast of Africa yield a fatty oil which has not yet been examined.[2] The seeds are known to the natives as "Krobonko seeds."

Physical and Chemical Characteristics of Koëme Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Refractive Index.		Observer.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	Butyro-refractometer.		
0·9180	+7	174·8 (?)	86·2	At °C.	Scale Divisions.	Thoms
				25	63·64	
				30	61·62	
		195·10	100·7	...	...	Lewkowitsch
		196·5[3]; 197·5[4]	88·5[3]; 88·3[4]	...	...	Bontoux

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Observer.
°C.	°C.	
41	44	Thoms
38·8 (Titer test)		Lewkowitsch

ELDERBERRY OIL

French—*Huile de sureau.* German—*Holunderbeerenöl.*
Italian—*Olio di sambuco.*

For tables of characteristics see p. 272.

This oil is obtained from the berries of the red elderberry, *Sambucus racemosa.*[5] A variety of the same oil was prepared by *Byers* and *Hopkins* from the berries of *Sambucus racemosa arborescens.*[6]

[1] J. R. Jackson, *Chemist and Druggist*, 1906, No. 1. [2] See p. 270, note 3.
[3] Extracted oil. [4] Expressed oil.
[5] Zellner, *Monatshefte f. Chemie*, 1902, 937 ; *Journ. Soc. Chem. Ind.* 1903, 101.
[6] H. G. Byers and P. Hopkins, *Journ. Amer. Chem. Soc.* 1902, 771.

Physical and Chemical Characteristics of Elderberry Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 20° C.	Observer.
0·9072	Byers and Hopkins	−8	Byers and Hopkins	0	Byers and Hopkins	209·3	Byers and Hopkins	81·44	Byers and Hopkins	1·54	Byers and Hopkins	1·472	Zellner
0·9171	Zellner	−3 to −4	Zellner			196·8	Zellner	89·5	Zellner	1·8	Zellner		
								110·6	Lewkowitsch	1·3	Lewkowitsch		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
91·75	Byers and Hopkins	38	Byers and Hopkins	204·8	Zellner	93	Zellner
95[1]	Zellner	43	Zellner			Liquid Fatty Acids.	
						120	Zellner

[1] This appears to be too high, in view of the Reichert-Meissl value found by the same observer.—(J. L.)

The solid fatty acids of elderberry oil consist, according to *Byers* and *Hopkins*, of palmitic acid exclusively. *Zellner* found in his specimen, besides palmitic acid (the chief constituent), small amounts of arachidic acid.

The liquid fatty acids, according to *Byers* and *Hopkins*, constitute 73·6 per cent of the mixed fatty acids, which agrees fairly well with the figure 71 found by *Zellner*. The distinct Reichert-Meissl value points to notable amounts of volatile fatty acids. *Byers* and *Hopkins* arrive at the following composition of the oil: palmitin, 22 per cent; olein and linolin, 73·6 per cent (of which olein forms 92·2 and linolin 7·8); caprin, caproin, and caprylin, 3·0 per cent.

Zellner concludes from the iodine value of the liquid fatty acids, viz. 120, that about two-thirds consist of oleic acid and the remainder of linolic acid; linolenic and isolinolenic acids could not be detected.

The specimen of oil examined by *Byers* and *Hopkins* contained 0·66 per cent of unsaponifiable matter, and had an acid value of 13·3. The acid value of *Zellner's* specimen was 3·2, the acetyl value 15·5; the mean molecular weight of the acetylated acids was 286, and their melting point 47°-49° C.

ELOZY OIL

French—*Huile de citron de mer*;[1] *huile d'Elozy.*
German—*Elozyöl.* Italian—*Olio di Elozy.*

This oil is obtained from the seeds of *Ximenia americana*, L., a tree widely distributed over tropical America, Africa, Asia,[2] and the Pacific Islands. In the Gaboon (West Africa), the tree is known under the names "Elozy" and "Zégué"; hence *Heckel* describes the oil under the name *Huile d'Elozy-Zégué.* In the catalogue of the Colonial section of the Paris Exhibition, 1879, the percentage of oil is given as 32·8. *Heckel* states that the seeds consist of 60 per cent of kernels and 40 per cent of husks. The kernels yield, on extraction with carbon bisulphide, 69 per cent of oil. *Suzzi*[3] found 65·6 per cent of oil in a specimen from Serae, in Erythrea (Italian East Africa). The oil had the following characteristics:—

Oil:—

Specific gravity at 15° C.	0·9165
Solidification point	+12 to +5° C.
Saponification value	155·3[4]
Iodine value	85·1
Maumené test	69° C.
Unsaponifiable matter	2 per cent

[1] Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Marseille, 1902, p. 27.
[2] East India.
[3] *I semi oleosi e gli oli*, published for the Milan Exhibition, 1906.
[4] These values require confirmation.

Fatty Acids:—

Solidifying point	45·5-42° C.
Melting point	45·5-48° C.
Neutralisation value	171·3[1]
Saponification value	171·8[1]
Mean molecular weight	326·5[1]

STAFF TREE OIL

French—*Huile de celastre.* German—*Celasteröl.*
Italian—*Olio di celastro.*

This oil has been prepared by *Suzzi*[2] from the seeds of *Celastrus Senegalensis*, which is widely distributed throughout Erythrea (Italian East Africa) where two species, viz. *C. Senegalensis* and *C. serratus*, occur. In the seeds collected in Hamasen *Suzzi* found 49·68 per cent of fatty matter which had the following characteristics:—

Oil:—

Specific gravity at 15°	0·9435
Solidifying point	−3 to −6° C.
Saponification value	223·5 (?)
Iodine value	86·7
Maumené test	77° C.

Fatty Acids:—

Solidifying point	32-29° C.
Melting point	34-37° C.
Neutralisation value	188·7
Saponification value	189·2
Mean molecular weight	296·5

The specimen of oil contained 10·12 per cent free fatty acids. The oil gives no colouration in the *Halphen* nor in the *Baudouin* test.

The seeds from the shrub *Celastrus paniculatus* yield a dark-red pungent oil from which "stearine" separates on standing. In Ceylon this oil is known as "Duhudu oil," and serves as a nerve stimulant; it is also used there for external application to sores.

OLIVE OIL

French—*Huile d'olive.* German—*Olivenöl.* Italian—*Olio d' oliva.*

For tables of characteristics see pp. 275-277.

Olive oil is prepared from the fruits of the olive tree, *Olea europea sativa*, L.

[1] These values require confirmation.
[2] *I semi oleosi e gli oli*, published for the Milan Exhibition, 1906.

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
12	0·9192	Saussure	At 2 turbid,	Chateau	191-196	Allen	82·8	Hübl	0·3	Medicus and Scheerer
15	0·9177	,,	at −6,		188·7-203 [1]	Dieterich	81·6-84·5	Dieterich		
15	0·9178 [1]	Clarke	"stearine"		185-196 [3]	De Negri	79·18-82·3	Villavechia		
15	0·9196 [2]	,,	separates		generally 190	and	79-88 [3]	De Negri and		
15	0·916-0·918 [3]	De Negri and Fabris	+3 to + 4 [8]	Bertain-chand		Fabris	generally 82	Fabris	Reichert-Meissl Value.	
					190·5-195 [10]	Oliveri	79-83·2 [10]	Oliveri		
15·5	0·9141-0·9171	Thomson and Ballantyne	+9 to +10 [9]	,,	190·9 [5]	Crossley and	78·9-86·9	Thomson and Ballantyne	0·6	Crossley and Le Sueur [5]
15·5	0·91747-0·91797 [4]	Moerck				Le Sueur	77·28-88·68 [4]	Lengfeld and Paparelli		
15·5 (water at 15·5 =1)	0·9203	Crossley and Le Sueur [5]			189·3-194·6 [4]	Tolman and Munson	80·7-91·5 [11]	Guozdenovič		
							83·3-86·1 [12]	Ferreira da Silva		
15·5	0·9155-0·9180 [6]	Tolman and Munson					93·67 [5]	Crossley and Le Sueur		
15·5	0·9162-0·9180 [7]	,,					78·6-87·2 [13]	Tortelli and Ruggeri		
18	0·9144-0·9163	Stilurell					84·0 [14]	,,		
18	0·9139-0·9141	Long					79·1 [15]	,,		
19	0·9134	,,					87-87·5 [16]	Ahrens & Hett		
20	0·9127	,,					91·4-91·7 [17]	,,		
21	0·9119-0·9121	,,					85·1 [4]	Tolman and Munson		
22	0·9112-0·9114	,,					81·5 [18]	,,		
23	0·9106-0·9117	,,					94·3 [19]	Thomson and Dunlop		
23	0·912-0·914	Dieterich					82·8 [20]	Shukoff		
24	0·9101-0·9099	Long					85 [21]	,,		
25	0·9094	,,					82·4-94·7 [22]	Archbutt		
30	0·9060	,,					82·4-90·4 [23]	,,		
35	0·9028	,,								
50	0·8932	Saussure								
94	0·8625	,,								

1 'Virgin oil. 2 Gallipoli oil. 3 Derived from observations on 203 samples. 4 Californian oils. 5 Oil from the Punjab.
6 18 Italian oils. 7 38 Californian oils. 8 Tunisian oils from the South (Gabès, Safsa, Djerba). 9 Tunisian oil from Sfax (cp. p. 279).
10 Derived from observations on 106 samples. 11 60 samples of Dalmatian oils (in one case even 92·8 was found). 12 Portuguese oils.
13 Spanish oils. 14 Greek oil. 15 Turkish oil. 16 Morocco oil from green olives (*Chem. Repert.* 1903, 241). 17 Morocco oil from black olives.
18 Italian oils. 19 Mogador oil. 20 Crimean oil. 21 Persian oil. 22 Tunisian oils. 23 Algerian oils.

Physical and Chemical Characteristics of Olive Oil—continued

Thermal Tests.				Refractive Index.			Viscosity in Redwood's Viscosimeter.	
Maumené Test.		Heat of Bromination.						
°C.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
41·5-45·5	Archbutt	15	Hehner and Mitchell	15	1·4698	Strohmer	312·3 [1]	Crossley and Le Sueur
35 [2 3] (mean)	De Negri and Fabris	14·3	Jenkins	15	1·4703 [5]	Guozdenovič		
45-47 [4]	Blasdale	13·55 to 14·5	Archbutt	15·5	1·4703-1·4713 [4 3]	Tolman and Munson		
44 [8]	Tortelli			20	1·4670-1·4705	Holde		
Specific Temperature Reaction.				60	1·4548	Thoerner		
89-95	Thomson and Ballantyne			Oleo-refractometer.				
				"Degrees."		Observer.		
				0 to 2		Jean		
				0 to +1·5		Bruyn and van Leent		
				+1 to +3·5 [6] at 22° C.		Pearmain		
				Butyro-refractometer.				
				At °C	"Degrees."	Observer.		
				15·5	67·3-68·5 [7]	Tolman and Munson		
				15·5	66·9-69·2 [4]	,,		
				25	62-62·8	Mansfeld		
				40	54·13-54·7	Bömer		
				40	56·4 [1]	Crossley and Le Sueur		

[1] Oil from the Punjab. [2] Derived from observations on 203 samples. [3] By Jean's thermelæometer. [4] Californian oils.
[5] 60 samples of Dalmatian oils (in one case the iodine value was 92·8). [6] 105 samples. [7] Italian oils. [8] Tortelli's thermoleometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At ° C.		Observer.	° C.	Observer.	C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60 °C.	Observer.
95·43	West-Knight	99 (water	0·8430	Allen	21·2	Hübl	26	Hübl	193	Thoerner	279·4	Allen	86·1	Morawski and	1·4410	Thoerner
94-96 [6]	Lengfeld and Paparelli	15·5=1) 100 (water	0·8749	Archbutt	21	Allen	26	Allen			286	Williams		Demski		
					Not below 22	Bach	23-24 to 26-27	Bensemann					90·2	Williams		
95·14 [1]	Crossley and Le Sueur	100=1)			23·5-24·6	Dieterich	26·5-28·5	Bach					87-88	Thoerner		
					22-17 [2]	De Negri and Fabris	24-27 [2]	De Negri and Fabris					Iodine Value of the Liquid Fatty Acids.		Refractive Index of the Liquid Fatty Acids.	
					21-22	Thoerner	19-23 [6]	Moerck								
					Titer Test.		Mostly below 28 [6]	Lengfeld and Paparelli					96·4-97	Bömer	Butyro-refractometer.	
					16·9-17·15	Lewkowitsch	26-28	Thoerner					92·8 [6]	Tolman and Munson	At 40° C.	
					17·1-17·8 [3]		21-26 [6]	Blasdale [7]					94·0 [8]	,,		
					18·6-19·7		21·6-29·3 [8]	Tolman and Munson					95·5-101·5 [9]	Tortelli and Ruggeri	42·7	Bömer
					19·45-20		19·2-31·0 [6]	,,					95·5-104·2 [10]	,,		
					23-25	,,							103·5 [11]	,,		
					20·1-21·2 [4]								96·3 [12]	,,		
					19·75-20·8								95·5-112 [13]	Bertainchand		
					21-21·87	,,										
					21·5-22·9											
					18·4-19·2											
					18·9-19·8											
					25·2-26·4 [5]	,,										

[1] Oil from the Punjab. [2] Derived from observations on 203 samples. [3] Finest Tuscan cream. [4] Commercial oil. [5] Gallipoli oil. [6] Californian oils.
[7] *Journ. Soc. Chem. Ind.* 1896, 206. [8] Italian oils. [9] 12 Italian oils, iodine values varied from 80·0 to 85·4. [10] 7 Spanish oils, iodine values varied from 78·6 to 87·2.
[11] Greek oil, iodine value 84·0. [12] Turkish oil, iodine value 79·1. [13] Tunisian oils; cp. p. 279.

The olive tree is most likely indigenous to Western Asia, but at an early date it was introduced into all the countries bordering on the Mediterranean. In Syria, especially in the neighbourhood of Aleppo and on Mount Lebanon, the olive tree is abundant, and has become completely naturalised in Greece, Italy, Spain, and the south of France. In Northern Africa, especially in Algeria and Tunis, the cultivation of the olive tree has reached considerable dimensions. Recently the cultivation of the olive tree has been introduced into California, South Africa, and Australia. The olive tree thrives best in a sub-tropical climate, and its successful cultivation extends in Europe as far north as latitude 44½°. In America it scarcely extends to latitude 34°.

Attempts have also been made in several parts of India to cultivate the olive tree, but although the tree grows well and flowers, the fruit seldom matures.

In Italy the young olive trees bear fruit two years after being planted, and after six years they become a source of income. The cultivation requires great attention, not only as regards weeding, but especially as regards the prevention of diseases peculiar to the olive tree. Noticeable amongst the diseases of the olive tree are the "pourridié," which affects the roots when they receive too much moisture, and "tuberculosis" (or "rogne") caused by *Bacillus oleæ*. The latter produces tumours which exhaust the tree and cause its death. Fungi which especially attack olive trees are: *Fumago salici* and *Cycloconium oleaginum* ("occhio di pavone"). The chief damage, however, is done to olives by insects, notably by the olive fly, *Mosca olivarum* ("mouche de l'olive"), also known as *Dacus oleæ*. Other insects which attack the olive tree are several species of cochineal, such as *Lecanium* (large cochineal), which assists the development of *Fumago salici*, *Psylle de l'olivier*, *Aspidiotis nerii*, *Parlatoria calianthina*, and *Chilicorus*. For further information the reader must be referred to the papers mentioned in the footnote.[1] With regard to the constituents of olive leaves and olive bark, cp. *Power* and *Tutin*.[2]

The olives intended for oil production are gathered just before the period of maturity, as the oil obtained from the barely ripe fruit is much superior in quality to that obtained from fully ripe or over-ripe fruits.

The proportion of oil in the fruit goes on increasing to the maximum found in the fruit which has reached complete maturity; it then decreases slowly. The ripe olives contain up to 70 per cent of oil. This figure is, however, an exceptional one, the fleshy part of the best cultivated olives containing only from 40-60 per cent of oil.

[1] Cp. *Rapport sur les cultures fruitières, et en particulier sur la culture de l'olivier*, Tunis, 1899; *Congrès oléicole et concours régional agricole de Sfax, 18 et 25 janvier 1904*, Tunis, 1904; J. Dugast, *L'Industrie oléicole* (*Encyclopédie scientifique*); L. Trabut et R. Marès, *L'Algérie agricole en 1906* ("Olivier," pp. 186-230), Alger, 1906; *Olives: Varieties and their Adaptation*, by George E. Colby (Bulletin No. 123); *Revision of Report on the Condition of Olive Culture in California*, by A. P. Hayne (Bulletin No. 129); *California Olive Oil: its Manufacture*, by G. W Shaw (Bulletin No. 158).

[2] *Proceed. Chem. Soc.* 1908, 117.

The Algerian olives vary in their proportion of oil within wide limits, from 10·03 per cent (Tlemcen olives, demi-grosses, *Telsi*) to 32·98 per cent in the Jemmap olives, greffées, *Garel*.

More recent analyses of the most important kinds of Tunisian olive oil, published by *Bertainchand*,[1] are briefly summarised in the following table :—

Olives from	Per cent of marc.
Région du Nord—	
Djebel Amar, Tebowika, Tunis, Zaghouan	24·0–39·0
Région du Sahel—	
Monastir, Kalaa-Srira	28.3–41·0
Région du Sfax	32
Région de Gafsa—	
Oasis de Gafsa	23·0–33·5
Région du Sud—	
Oasis d'el Oudiana, Gabès, Djerba, Zarzis	22·5–49·0

The Californian olives also yield much smaller quantities of oil than the best cultivated European ones. Among the large number of analyses published by the Agricultural Experiment Station of the University of California we find the lowest percentage, 11·23 (in the locality of Sacramento), and the highest, 22·3 (in Oakdale), both olives being varieties of the "mission" olive, the oldest olive grown in the State. The "ruabra" olive, imported into California from France, yields up to 27·91 per cent (district of Lincoln).

In the determination of the proportion of oil in olives or olive pulp, carbon bisulphide should be used in preference to ether, as the latter dissolves other (non-fatty) substances together with the oil.[2]

The technical processes employed for the production of olive oil furnish one of the best instances for the correctness of the statement made in the opening of Chap. XIII. The very oldest and crudest processes still survive in those districts of Algeria and Tunis[3] which

[1] Dugast, *L'Industrie oléicole*, Paris, 1905.

[2] Cp. Peano, *Journ. Soc. Chem. Ind.* 1903, 35.

[3] The culture of the olive tree in Tunis dates from about the first century B.C. It was very prosperous until the sixth invasion of the Arabs (693-694 A.D.), who destroyed a great number of plantations. During a later invasion of the Arabs in 1048 the olive trees of the Sfax district were entirely destroyed. Fresh plantations were not made before 1800-1810. Since then the olive culture has developed greatly, so that the number of olive trees in Tunis is estimated to amount at present to 11,222,525. In the Sfax district, which is the most important and progressive in Tunis, two kinds of olives are planted for eating purposes : (1) the "mellahi," a round fruit reaching sometimes the size of a small apricot, which is picked green for salting ; and (2) the "nab," which is smaller than the former and has an oval shape. The olives grown for oil-producing purposes are of the "chemlali" type. This fruit, which is much smaller than the "mellahi" and "nab," grows over the whole of North Africa. Two-thirds of the oil produced in Tunis

are farthest removed from the coast. The difficulty which especially besets the production of olive oil is the circumstance that it is impossible to gather all the fruit at the most favourable time and crush it immediately. Hence the fruit has to be preserved until it can be worked up. Consequently fermentation, with subsequent decomposition of the oil, sets in (see below). A number of methods have been proposed for preserving the fruits; the best seems to be storage in well-ventilated rooms, the olives being exposed to the air in shallow layers. Where this is not possible, recourse is had to preservation in sea-water or brine, with exclusion of air.[1]

In this work only the most modern methods adapted to large scale working can be considered. They consist in working up the olives by the mixed process (p. 26), *i.e.* by expression and subsequent extraction. Therefore, reference can only be made in passing to processes such as those proposed by *Kuess*,[2] *Funaro*,[3] *Tanquerel*,[4] and *Miguel del Prado*.[5]

The machinery employed in the production of olive oil varies considerably in the various countries, although in the main it is the same kind as that described generally in Chap. XIII. For a description of the special apparatus employed in Tunis and California (which have been adapted from the methods worked in France and Italy) the reader must be referred to the special work by *Dugast* and the "Bulletins" published by the *Agricultural College of the University of California*. It may suffice here to give in a general way an account of an ideal process producing all kinds of olive oil from the very finest down to the very lowest, and embracing the various methods in vogue in the different countries.

The very finest oils are obtained from *hand-picked fruits*[6] by first crushing them in a mill without breaking the kernels. Exceptionally fine qualities are prepared by peeling hand-picked fruits and pressing lightly, after carefully removing the kernels. The crushed marc is then expressed in a hydraulic press; the oil so obtained ranks as the best edible oil—*huile vierge, huile surfine*.[7] Commercial brands of this quality are "Provence Oil," "Aix Oil," "Nice Oil," "Var Oil." The oils sold as "Finest Tuscan Cream," "Riviera Oils" (Genoa),

comes from Arab mills, where the most rudimentary processes still survive, the mill being a mere roller turning inside a cylindrical basin; the roller is driven by animal power. The fruits and stones, reduced to a pulp, are spread over round pieces of matting made of esparto grass which are put into a wooden press, when a mixture of water and oil exudes. If the olives cannot be worked up immediately they are placed in a dark room and each layer of olives is covered with salt.

[1] Klein, *Zeit. f. ang. Chemie*, 1898, 848; Mastbaum, *Chem. Rev.* 1904, No. 345.

[2] French patent 291,559, 1899.

[3] *Statz. Exper. Agrar. Ital.* 1902, p. 916.

[4] French patent 345,849.

[5] French patent 365,187, 1906.

[6] The method of knocking off the fruits by poles leads to bruising of the olives, which in its turn leads to the obtainment of inferior oil.

[7] Marcille (*Bulletin de la Direction de l'Agriculture du Commerce et de la Colonisation, Tunis*, 1907, 531) points out that the epidermis of olives is richer in vegetable acids, has a harsher taste, and contains larger amounts of tanning and ethereal substances than the marc. He further showed that these foreign substances pass to a greater extent into the olive oil, if the pulp is more finely broken up and the pressure higher than is practised in the case of peeled olives. The superiority of the "virgin oil" is therefore easily explained and does not seem to be conditioned by the removal of the kernels.

"Bari Oils" may also be ranked amongst the best edible oils, although they are distinctly lower in value than the south of France oils, and come nearer the following somewhat inferior quality. This is obtained by pouring some cold water on the marc, after the pressure in the hydraulic press has been released, and pressing again. Such inferior oil is also sold as an edible oil either alone or mixed with the oil of the first expression—"Salad Oil," *huile fine, huile de table ordinaire.*

The pulp is now taken out of the press, mixed with *hot* water, and pressed again *once* or *twice.* Thus the bright oils used for various technical purposes—*huile de commerce, huile d'industrie, huile échaudée* —are obtained. They are especially used for lubricating purposes, as burning oils, and for soap-making, under the names *huile lampante, huile à brûler, huile à fabrique ; olii lavate* (washed oils).

All the oils obtained so far are somewhat turbid and are brightened by washing and filtering.[1] In the case of the edible oils, settling and subsequent filtration suffice for the production of merchantable oils. Most of the technical oils are treated in the same way ; oils of lower qualities are refined in the same manner as rape oil, by treatment with sulphuric acid.

In most of the smaller works the kernels are not removed and are crushed together with the fruit. In large establishments, however, the kernels are removed and crushed separately, yielding the olive kernel oil, described p. 298. Opinions, however, differ as to the advantage this procedure is said to offer. At any rate for lower-class edible oils the removal of the kernels seems to make no difference in the quality of the oil.[2]

The repeatedly pressed pulp—grignons (*bucchiette, polpè*)—still contains a considerable amount of oil, varying from 10-22 per cent in different samples examined by the author. The pulp is now beaten with hot water in special mills—*moulins de ressence*—resembling the well-known edge-runners. The oil cells are thereby further broken up ; the ground mass, together with the water, is then allowed to run into a series of vessels, arranged in tiers, where the water separates from the oil and broken cellular tissues. The oil and the tissue rise to the surface, where they are skimmed off, whilst the heavier kernels fall to the bottom. The latter are known as *grignon marc blanc.* The emulsion of oil and cellular tissue, which has been skimmed off the water, and is known as *grignon marc noir,* is heated up and subjected to a fresh expression in a hydraulic press. The oil so obtained is termed *huile de ressence,* and the pressed residue is known as *tourteau de ressence.* The *huile de ressence* is allowed to rest in large tanks at a somewhat elevated temperature, when a clear oil separates on the top—*huile claire de ressence*—and a lower layer of thicker oil—"Olive

[1] A special apparatus for washing olive oil has been patented by V. Coq, French patent 360,733, 21st December 1905.

[2] Cp. Passerini, *Staz. sperim. agr. italiani,* 37 (1904), 600. Marcille (*Bulletin de la Direction de l'Agriculture du Commerce et de la Colonisation,* 1907) discusses this subject exhaustively, and shows that the previous separation of the kernels from the pulp is an unnecessary operation and only leads to higher working costs.

Oil Grease" (*pâte de ressence*)—settles out. Such an olive oil grease examined in the author's laboratory contained 48 per cent of free fatty acids. In consequence of the repeated treatments, this oil has become oxidised to some extent. A specimen of *pâte de ressence* examined by *Merklen*[1] contained about 10 per cent of lactones.

In some establishments the marc, instead of being boiled up with water, is thrown into pits where the pulp undergoes a kind of fermentation (see below under "Free Fatty Acids"), whereby the oil is set free and gradually rises to the top. Oil of this kind is known as *huile d'enfer*, *huile d'infect*, *Nachmühlenöl*, *Höllenöl*, *Sottochiari*. The name *huile d'enfer* is applied also to oil which has settled out from the waters obtained from the press after moistening and boiling the pulp, which has been stored in underground cisterns, "*enfers*." To this class of oils belong the *bagassa* (*bagasse*) oils, which are obtained from fermented marc, principally in Portugal. These oils contain as much as 60-70 per cent of free fatty acids.

"*Tournant oil*" is a commercial product of the quality of the "*huiles d'enfer*," obtained from the fermented marc of expressed olives; it contains a considerable quantity (up to 26 per cent) of free fatty acids, and, therefore, forms a very complete emulsion with a solution of sodium carbonate, which constitutes its value as Turkey-red oil (Chap. XV.).

The cake remaining after the removal of the *huile de ressence*, termed *tourteau de ressence*, or *sanza*, is finally deprived of its last content of oil by extracting with solvents, sometimes after a preliminary drying. The solvent most usually employed in France and Italy is carbon bisulphide. Hence, these oils are termed sulphocarbon oils, sulphur olive oils, *huiles de pulpes d'olive sulfurées*, *huiles de pulpes d'olive*, *huiles d'olive sulfurées*; *Sulfuröle*. They have a deep green colour, due to the chlorophyll which has been extracted by the solvent, and contain the more solid portion of olive oil which has remained in the pulp. The proportion of lactones in these low-class oils is, however, small owing to the slight solubility of lactones in carbon bisulphide (or petroleum ether). *Merklen*[2] states that sulphur oils contain as a maximum 1 per cent of lactones. Some such sulphur oils (Italian and Syrian) examined by the author (Vol. I. Chap. V.) contained from 48 to 64 per cent of free fatty acids. These oils are characterised by containing organic sulphur compounds. (For the detection of sulphur see Vol. I. Chap. IV.) For the bleaching of such oils by means of organic peroxides, cp. French patent 378,515 (*Vereinigte chemische Werke*, Charlottenburg).

Suggestions have been recently made aiming at the extraction of the *sanza* with carbon tetrachloride,[3] but at the present price this solvent cannot compete with the cheaper carbon bisulphide.

[2] *Études sur la constitution des savons de commerce*, Marseille, 1906, p. 106.

[2] *Ibid.*

[3] Cp. P. Bernard, French patent 338,354. A description of the process and a calculation of cost had been given by R. Jürgensen (*Zeit. f. ang. Chem.* 1906, 1546), who curiously enough states that the apparatus is made entirely of iron, and is not attacked by carbon tetrachoride.

Instead of extracting with carbon bisulphide *Rodolphe Bernard* proposes to treat the intimate mixture of pulp and water—*crasse d'huile d'olive*—with concentrated sulphuric acid in order to break the emulsion.[1] This method cannot compete with the extraction process.

The water—*eau de végétation*—which collects in the pits after decantation of the supernatant oil is a black acid liquid known as "margines," *Agua ruça*. The specific gravity varies from 1·050 to 1·060. It contains small amounts of nitrogenous substances, potash salts, and other extractive substances from the flesh of the olive. Hitherto this liquid has not been used commercially. Proposals to work it up for the potash it contains have not been carried out on a large scale.[2]

The extracted cake is sold as manure. The press residues, which have yielded superior kinds of olive oil, may yield cakes for feeding cattle; but as the oil, which can be easily recovered by extraction—about ten per cent of the residues,—is too valuable, olive cakes for feeding cattle have not yet come into the market. Moreover, considerable quantities of nitrogenous substances and potash salts are lost to the cakes by having passed into the "margines"[3] (see above), and furthermore the olive cakes become so rapidly rancid that they would have to be used up in the fresh state. Still, small quantities of the pressed residues are fed locally to pigs. *Miguel del Prado* in his above-mentioned French patent 365,187, especially claims the production of feeding cakes.

Various proposals have been made to work up the extracted olive oil residues by destructive distillation (*Juergensen*, Paris Congress, 1900). *Guerrero de Smirnoff*[4] has recently taken out a patent to work the residues for the production of char (carbon) on the one hand and ammoniacal salts, acetates, methyalcohol, etc., on the other hand, by a process of dry distillation.

The commercial importance in the Mediterranean of olive oil may be gathered from the following table :—

[1] French patent 325,966.

[2] Cp. *Les Huiles d'olives de Tunisie et l'utilisation des margines*, E. Milliau, Bertainchand, et F. Malet, *Moniteur Scientifique*, 1900, 508 ; E. Milliau, *Bullet. de la Direction de l'Agriculture et de la Commerce*, Tunis, 1903, p. 488.

[3] Cp. O. Klein, *Zeit. f. ang. Chem.* 1900, 635.

[4] French patent 353,970, 1905. Cp. also Marchette and Molco, *Chem. Ztg.* 1906, 972.

Mean Production of Olive Oil during 1900 *to* 1906 *in the Mediterranean Basin* [1]

	Hectolitres.
Spain	2,660,000
Italy [2]	2,604,330
Asiatic Turkey	1,980,000
Greece [3]	601,411
Portugal	398,150
France	333,000
Tunis	301,100
Algeria	231,000
Austria	65,366
	9,174,357, or about 820,000 tons.

It will be seen from the above table that France produces a comparatively small amount of olive oil. Large quantities, however, are imported, especially from Algeria and Tunis, to be mixed with home-grown oil, a portion of which is again exported. The following table gives the French imports and exports of olive oil during the last few years :—

Olive Oil Imports into, and Exports from, France

Double (metric) hundredweights

	1900.	1901.	1902.	1903.	1904.	1905.	1906.
Imports—							
"Commerce général"	276,238	285,937	380,515	295,887	471,859	282,160	410,257
"Commerce spécial"	167,234	170,825	200,141	181,120	295,024	187,045	252,632
Exports—							
"Commerce général"	170,026	187,830	171,766	172,480	195,968	219,963	228,198
"Commerce spécial"	66,020	72,597	43,952	46,563	53,959	7,600	

The imports of olive oil into England (chiefly from Italy, Spain, and France) are given in the following table [4] :—

Year.	Tons.	Year.	Tons.
1866	16,935	1900	12,044
1870	23,202	1902	18,978
1875	35,453	1903	14,485
1880	20,260	1904	15,010
1885	24,227	1905	12,042
1890	20,187	1906	14,386
1895	14,834	1907	12,328

[1] Statistics of the French Ministry of Agriculture.

[2] For details of export, see Appendix.

[3] For a report on the production of olive oil in Crete, cp. *Zeit. f. ang. Chem.* 1907, 1917.

[4] For the details of the imports during the years 1902-1906 see Appendix.

In the Southern Caucasus the production of high-class olive oils is now being taken in hand. The olive oil produced there represents two distinct varieties having different taste and colour. They are known as "Artwin" and "Barku" olive oils.

As regards California, in the year 1899 two and a half million olive trees were counted, which were judged to be able to furnish over two million gallons of oil, not counting the olives required for preserving. The quantity named has, however, not been produced, as the consumption of olive oil in the States is covered to the greatest extent by the importation of olive oil from France, Italy, and Spain; smaller quantities being imported from Greece, as also from Portugal and Austria. The products of the last-named countries are not only cheaper—notwithstanding import duty—but are also preferred on account of their flavour; for most of the oil produced in California has still a harsh flavour. This difficulty militates against the more rapid expansion of the industry at present, but it will, no doubt, be overcome by the great efforts which are being made by the olive growers under the ægis of the *Agricultural Experiment Station of the University of California.*

The production of oil in South Australia is also increasing rapidly. Whilst in 1901, 6520 gallons only were manufactured, the colony possessed, in 1902, 66,852 olive trees yielding 11,327 gallons of oil.

From the above sketch of the processes employed for the production of olive oil it will be easily gathered that the specimens found in commerce must vary to a considerable extent, their quality depending on many circumstances, such as the variety of the olive tree itself (Italy alone produces about 300 varieties of the olive), the climatic conditions, the nature of the soil, the degree of ripeness of the fruit, the manner of gathering it, the mode of expressing, etc. The value of the edible oils in particular depends on their limpidity, colour, and especially on their taste.

Limpidity is one of the chief properties a good edible oil should possess. This is, in the first instance, obtained by proper filtering and then by allowing the oil to deposit all the "stearine" that will settle out at such temperatures as the oil may have to withstand. An oil which will remain clear at 10° C. will always command a higher price than an oil which becomes turbid or even sets to a pasty mass at this temperature.

The **colour** of olive oil varies considerably; the commercial oils are of all shades from colourless to golden-yellow; a green colour is very pronounced in the low-class olive oils, due to dissolved chlorophyll.

The **taste** of olive oil in its purest state is bland and pleasant; it varies, however, with the locality where the fruit has been grown. Thus, the oils obtained from Tuscan fruits possess a decidedly more agreeable taste than those from Ligurian olives. Therefore purity alone is not a sufficient test in the valuation of a sample of olive oil. An oil may be free from adulteration and still be an inferior oil, on

account of its rank and nauseous taste. *Canzoneri*[1] isolated from the bitter and harsh Puglia olive oils eugenol, to which he ascribes the harsh taste; and further catechol, gallic acid, tannin, and an unknown substance, which are said to cause the bitter taste. It is noteworthy that the objectionable taste disappears in time. The large quantities of edible oils produced in Tunis are frequently admixed with the best brands of French and Italian edible oils, in order to mask their somewhat harsh taste.

The solid fatty acids of olive oil consist of palmitic and a minute proportion of arachidic acids. *Hehner* and *Mitchell*[2] did not obtain any stearic acid crystals from olive oil; therefore absence of stearin must be taken as proven.

Holde[3] tried to resolve the mixed solid fatty acids of olive oil into their components and obtained a small quantity of an acid of the melting point 72-72·8° C. and molecular weight 368·7. It is doubtful whether this acid is lignoceric acid (melting point 80·5° and molecular weight 368). This disposes of the statement previously made by *Holde* and *Stange*[4] that olive oil contains "oleodaturin," the "daturic" acid having been found to represent a mixture of acids (cp. Vol. I. Chap. III.).

Tolman and *Munson*[5] found in the examination of eighteen samples of genuine Italian olive oils as the lowest amount of solid fatty acids obtainable by the lead-salt-ether method 5·0 per cent (in a Tuscany oil of the iodine value 80·7), and as the highest amount 17·72 per cent (in a Bari oil of the iodine value 81·2), whereas in the corresponding examination of thirty-eight Californian olive oils the lowest amount found was 2·0 per cent of solid fatty acids (in a Santa Barbara oil of the iodine value 84·7), and the highest amount 12·96 per cent (in a Cloverdale oil of the iodine value 81·9).

These numbers seem to be somewhat conflicting, but they dispose finally of the statement, so frequently found in text-books, that olive oil contains, as a rule, about 28 per cent of solid glycerides.

Tunisian oils from Sfax contain, according to *Bertainchand*,[6] up to 25 per cent of solid fatty acids. The high amount of solid glycerides causes these oils to deposit "stearine" at + 9° to + 10° C. The difference in composition of the various kinds of Tunisian oils, as regards solid fatty acids, is exemplified by the following table:—

	Solid Fatty Acids.	Liquid Fatty Acids.
Olive oil from the North (Tunis, Bizerte, Cap-Bon, Medjerdah)	Per cent. 15	Per cent. 85
Oil from the Centre (Sousse, Mahdia, Monastir)	21	79
Oil from Sfax	25	75
Oils from the South (Gabès, Gafsa, Djerba)	15	85

[1] *Gaz. Chim. Ital.* 27. ii. 1.
[2] *Analyst*, 1896, 328.
[3] Holde, *Berichte*, 1905, 1250.
[4] *Berichte*, 1901, 2406.
[5] *Journ. Amer. Chem. Soc.* 1903, 956.
[6] *Bull. de la Direction de l'Agric. et du Comm. Tunis*, viii. (1903), 167.

In order to free the Sfax oils from the excess of glycerides of solid fatty acids, it is necessary to "demargarinate" them (cp. Chap. XIII.).

The liquid glycerides were formerly considered to be practically pure olein (notwithstanding a conjecture of *Mulder* as to the presence of an unsaturated fatty acid other than oleic), but *Hazura* and *Grüssner* have shown that the liquid portion of olive oil contains, besides oleic acid, the less saturated linolic acid, approximately in the proportion of 93 oleic acid to 7 linolic acid. From this proportion the iodine value of the liquid fatty acids would be calculated to be 96·56; this number is in agreement with most of the values found experimentally.

Milliau, *Bertainchand*, and *Malet*[1] found in Tunisian olive oils from Bizerte, Tunis, Sousse, Sfax, and Gafsa respectively the following iodine values of the liquid fatty acids: 105·7; 113·4; 116·5; 118·2; and 106·9. The more recent analyses published by *Bertainchand* give the following iodine values of the liquid fatty acids of olive oils from the districts: Région du Nord, 95·48-107·66; Région du Sahel, 98·37-109·32; Région de Sfax, 103·74; Région de Gafsa, 103·5-111·95; Région du Sud, 95·37-105·4.

The *minimum* iodine value of the liquid fatty acids in the above-mentioned eighteen Italian olive oils, examined by *Tolman* and *Munson*,[2] was 89·8[3] (Tuscany oil of the iodine value 80·7), and the *maximum* 98·4 (in an Abruzzi oil containing 13·51 per cent of solid fatty acids). The lowest iodine value of the liquid fatty acids of the thirty-eight Californian olive oils was 88·9 (in a Napa oil of second expression), and the highest iodine value of the liquid fatty acids 99·6 (in a Chico oil containing 5·12 per cent of solid fatty acids).

On reducing olive oil with hydrogen in the presence of colloidal palladium in the cold, *Paal* and *Roth*[4] obtained a solid fat, softening at 43° C. and completely liquid at 47° C. The iodine value of the reduced glyceride was 9. The reduction took place with much greater difficulty than in the case of castor oil, and the amount of hydrogen absorbed was in this case three times the theoretical one (cp. Vol. I. Chap. I.).

Free Fatty Acids.—The best and finest edible oils should contain practically no free fatty acids. Even the salad oils are practically devoid of free fatty acids, as they contain no more than 0·2-0·5 per cent of free fatty acids. The lower-class oils exhibit larger amounts. The longer the oil is allowed to remain in contact with the fleshy part of the fruit the greater will become the hydrolysis of the oil, with consequent production of free fatty acids (cp. Vol. I. Chap. I.). The exceedingly rapid decomposition olive oil undergoes when left in contact with the marc, is undoubtedly due to a ferment. Indeed, *Tolomei*[5] has isolated a ferment which he terms "olease," to the

[1] *Bull. de la Direction de l'Agric. et du Comm. Tunis*, viii. (1903), 167.
[2] *Journ. Amer. Chem. Soc.* 1903, 956.
[3] This number does not necessarily point to the absence of linolic acid, since the "liquid" fatty acids very likely contained some saturated fatty acids.
[4] *Berichte*, 1908, 2283.
[5] *Atti dei Lincei*, 1896.

action of which he ascribes the rapid fermentation which takes place in stored marc. Besides this ferment, fungi, such as *Penicillium glaucum* and *Saccharomyces olei* (discovered by *van Tieghem*) contribute to the hydrolysis, they on their part most likely producing an enzyme. It therefore follows that in order to prevent hydrolysis the oil must be separated as carefully as possible from the putrescible marc. Once hydrolysis has set in, olive oil, like other oils, becomes rancid when exposed to the atmosphere. The extraordinarily high percentage of fatty acids in the *bagasse* oils, as also in sulphur oils (see p. 282), is thus readily explained. From a very rancid olive oil *Scala* [1] isolated œnanthylic aldehyde; formic, acetic, butyric, œnanthylic acids, and also azelaic and suberic acids. The acetyl value of an old commercial oil was found by *Lewkowitsch* to be 10·6. In the following table some further data are given.

Free Fatty Acids in Olive Oil

Description of Sample.	Number of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent.	
Edible oil	1	1·17	Salkowski
,, ,,	1	1·66	Rechenberg
Commercial oil	49	Less than 5	Archbutt
,, ,,	66	5-10	,,
,, ,,	44	10-15	,,
,, ,,	1	20-25	,,
,, ,,	11	3·86-11·28	Thomson and Ballantyne
,, ,, (Syrian)	1	23·88	,,
,, ,, (Californian)	3	1·55-8·33	Moerck
,, ,, (European)	3	0·97-1·09	,,
,, ,, (Italian)	18	0·57-2·79	Tolman and Munson
,, ,, (Californian)	38	0·20-3·51	,,

The following table, culled from observations of *Mastbaum*,[2] shows in an instructive manner the changes which the oil undergoes in stored olives. The olives were "bagassa" olives which had to be stored immediately, owing to the impossibility of working them up.

Oil from	Free Fatty Acids.	Iodine Value.	Acetyl Value.
	Per cent.		
Fresh olives	0·33	76·3	4·8
Olives preserved five months—			
(*a*) In brine, without removing the brine	6·72	76·6	10·1
(*b*) In running water	6·08	76·7	15·6
(*c*) In brine, the brine being removed at intervals	23·26	77·2	25·1
(*d*) By drying	49·02	77·7	30·9

[1] *Staz. Sper. Agr. Ital.* 30, 613.

[2] *Chem. Rev.* 1904, 66; cp. also Lewkowitsch, *Jahrb. der Chemie*, xiv. p. 430.

Olive oils containing more than 5 per cent of free fatty acids are not suitable for lubricating purposes; they are also unsuitable for burning, as they cause charring of the wick.

The **unsaponifiable matter** in olive oil, as in all vegetable oils, is phytosterol. *Thomson* and *Ballantyne* found in 12 samples of oil the proportions of unsaponifiable matter lying between 1·04 and 1·42 per cent, which is somewhat higher than the *minimum* and *maximum* amounts recorded for a large number of samples, viz. 0·46 and 1·0 per cent respectively.

Olive oil is the type of a non-drying oil. Hence it shows in the *Maumené* test, as also in the heat of bromination test, the smallest rise of temperature of all vegetable oils, and it absorbs also the lowest amount of oxygen in *Livache's* test (Chap. VII.). At higher temperatures olive oil becomes oxidised if spread on lead powder.

Experiments made by *Procter* and *Holmes*[1] with a view to ascertaining the influence which blowing with air at 100° C. exercises, gave the results stated in the following table :—

	Hours.	Specific Gravity.	Refractive Index.	Iodine Value.
Original oil . . .	...	0·912	1·4695	86·0
Blown oil . . .	3	0·913	1·4696	86·0
,, ,, . . .	6	0·913	1·4697	82·0
,, ,, . . .	9	0·913	1·4698	80·0
,, ,, . . .	12	0·913	1·4699	80·0
,, ,, . . .	15	0·914	1·4700	79·0
,, ,, . . .	18	0·914	1·4700	79·0
,, ,, . . .	21	0·915	1·4700	79·0
,, ,, . . .	24	0·918	1·4701	76·0

On account of its comparatively high price olive oil is adulterated to an enormous extent. How far the blending of various olive oils of different qualities should be considered as an adulteration must be decided in each given case. Undoubtedly the "finest Nice oil," which has been prepared by blending a genuine Nice oil with Tunisian oils or other olive oils, must be considered as of inferior quality. But since purely chemical tests are incapable of deciding this question, which is readily settled by the taste and by taste alone, an analyst without special experience in that direction would have to pass such oil as genuine Nice oil.

In the following lines I can, therefore, only consider adulteration with other oils than olive oil. The oils that are usually admixed with it are sesamé, rape, cotton seed, poppy seed, arachis and lard oils. The olive oils sold under fancy names are, as a rule, adulterated.

The tables of characteristics contain a very exhaustive list of numbers, so that by carefully scrutinising them, methods for the

[1] *Journ. Soc. Chem. Ind.* 1905, 1287.

examination of a given sample, suspected of being adulterated, can be derived. It is, therefore, only necessary to emphasise the most salient points.

The **specific gravity** of olive oil ranges from 0·916 to 0·918 at 15° C., but may rise to 0·920 in the case of commercial oils expressed at a higher temperature. Oils of high specific gravity usually exhibit a dark colour. The influence of free fatty acids on the specific gravity has been pointed out already (Vol. I. Chap. V.). If the specific gravity of a pale olive oil be found higher than 0·918, it must be looked upon with suspicion, *i.e.* as possibly adulterated with *sesamé*, *cotton seed*, or *poppy seed oils*. Sophistication with *rape* or *arachis oil* is not indicated by the specific gravity, the differences in the respective gravities being too insignificant.

The **melting and solidifying points of the fatty acids** (or titer test) will also furnish useful indications as to the purity of an olive oil. But it would be hazardous to draw too far-reaching results from this test. Hence the tabulated observations recorded in the second edition of this work have been omitted here.

The **iodine test** constitutes the most valuable means of detecting adulteration. Olive oil has nearly the lowest iodine absorption of any oil that might be used for adulteration. As a rule, the iodine value of olive oil should lie between 81·6 to 84·5. There occur, however, undoubtedly genuine oils, the iodine values of which exceed these numbers. Thus the oil from the Colombaio olive reaches 86, oil from some Portuguese varieties (sevilhana, mançanilha, cordovil) 87 (*Klein*), Californian oils 88, and in the case of a Dalmatian oil as high a figure as 92·8 was obtained (this has been even exceeded by an olive oil from the Punjab, of the iodine value 93·67, and by a Magador oil [1] absorbing 94·3 per cent of iodine). Still, these cases are notable exceptions, and an oil with an iodine value exceeding 85 must, as a rule, be looked upon with suspicion. With regard to Tunisian and Algerian oils, the table given on p. 294 shows that genuine oils, having what may be termed the normal iodine value of olive oil, occur side by side with oils which are characterised by exceptionally high iodine values. It would, however, not be permissible to generalise as *Marcille* [2] has done, who from a systematic examination of genuine olive oils produced in Tunis, concludes that the iodine value from 90 to 92 may be taken as characteristic of this class of oil.

Paparelli [3] studied the causes of the variability of the iodine values, and arrived at the following conclusions:—The more mature are the olives the higher is the iodine absorption of the oil. Old and rancid oil has generally a slightly lower number than fresh oil. The method of preparing the oil has also its influence. Oil from the pulp absorbs slightly less iodine than that obtained by grinding pulp and "pits" together; oils extracted by solvents show lower values than expressed oils; again, oils from pits are characterised by higher numbers than

[1] Thomson and Dunlop, *Analyst*, 1906, 282.
[2] *Ann. Chim. anal. appl.*, 1907, 12, 188-191.
[3] *Journ. Soc. Chem. Ind.* 1892, 848.

those extracted from the fruit. The greatest variation, however, is found to be due to the variety of the olive tree from which the fruit is obtained.

If there is reason to exclude abnormal oils, a high iodine absorption may indicate adulteration with as little as 5 per cent of a *drying oil* (poppy seed, hemp seed oil) or 15 per cent of *sesamé*, *cotton seed*, and *rape oils*. Less positive results are obtained in the presence of *arachis oil*, since the lowest values recorded for that oil almost coincide with the highest value observed for olive oil.

It may be pointed out here that the iodine values of the semi-solid and of the liquid portions into which olive oil separates on partial solidification almost coincide (*Goldberg*).[1]

The **saponification value** will only lead to definite results (in the absence of mineral oils) if large quantities of *rape oil* have been admixed with olive oil.

In the **elaïdin test** olive oil yields of all oils the hardest elaïdin, and also requires the shortest time for solidification. The elaïdin reaction can only be used as a preliminary test. The effect of an addition of rape or cotton seed oil to olive oil is shown in the following table, compiled from numbers published by *Archbutt*[2]:—

Kind of Oil.	Minutes required for Solidification, at 25° C.	Consistence.
Olive oil	230	Hard, but penetrable
Olive oil + 10 per cent of rape oil .	320	Buttery
,, +20 ,, ,, .	From 9 to 11½ hours	Buttery
,, +10 ,, cotton seed oil	From 9 to 11½ hours	Very soft butter
,, +20 ,, ,,	More than 11½ hours	Very soft butter

It has been proposed to measure the effect of a foreign oil on the hardness of the elaïdin quantitatively by using *Legler's* method (Chap. V.), but it should be borne in mind that, according to *Gintl*, olive oil, after exposure to sunlight for a fortnight, no longer gives a solid elaïdin. *Farnsteiner*[3] has shown that the amount of oleic acid that is converted into elaïdic acid depends very much on the conditions under which nitrous acid acts on the oil. Indeed, when determining the amount of liquid fatty acids that had not been converted into elaïdic acid (by means of the lead-salt-benzene method), so widely differing results were obtained that the hope of basing a quantitative method upon it must be abandoned at present.

The **thermal reactions** lead to lower values than in the case of any other vegetable oil. *Lengfeld* and *Paparelli* assert that there exists a proportionality between the iodine number and the **Maumené test** of various olive oils. They obtained for fourteen oils numbers varying from 33·5° to 41° C., the oil having the highest iodine

[1] *Journ. Soc. Chem Ind.* 1897, 447. [2] *Ibid.* 1886, 308.
[3] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1899, 8.

absorption also causing the greatest rise of temperature. Their results, arranged by the author according to the iodine values, do not, however, bear out fully the correctness of this rule.

Olive Oil. No.	Iodine Value. Per cent.	Maumené Test. °C.
1	77·28	35
2	78·42	33·5
3	78·51	33·5
4	78·52	34
5	79·50	36
6	79·53	34·5
7	80·80	37
8	81·45	38
9	81·50	35
10	81·70	34
11	83·35	37·5
12	85·44	36·5
13	87·15	41

Tortelli[1] claims that he obtains with his thermoleometer such great accuracy in the *Maumené* test that the determination of the iodine value is thereby rendered superfluous. In the author's opinion this conclusion is tantamount to begging the question.[2] Moreover, *Tortelli* overlooks adulteration with animal oils.

The proportionality between iodine number and **heat of bromination test** shows in a general way the same regularity; this will be seen from the numbers given in the following table (*Archbutt*[3]):—

Olive Oil.	Iodine Value. Per cent.	Heat of Bromination. °C.
Malaga	78·4	14·2
...	78·7	13·55
...	78·9	13·8
Malaga	79·3	13·8
...	81·4	14·2
...	81·4	14·35
Gallipoli	82·0	14·4
,,	82·1	14·5
,,	82·5	14·5
...	84·2	14·45

An examination of the **unsaponifiable matter** in olive oil[4] will be required if admixture of lard oil be suspected. The presence of the latter would be unmistakably detected by the phytosteryl acetate test. The alcohol contained in the unsaponifiable matter from olive

[1] *Bolletino Chimico Formaceutico*, 1904, 193.
[2] Lewkowitsch, *Jahrbuch der Chemie*, xiv. 438.
[3] *Journ. Soc. Chem. Ind.* 1897, 311.
[4] It should be noted that in Germany olive oil is "denatured" with rosemary oil, which of course increases the amount of unsaponifiable matter.

oil melts at 135·5°-136·5° C. (*Bömer*), 135°-135·5° C. (*Gill* and *Tufts*). Its acetate melts at 120·3°-120·7° C. (*Gill* and *Tufts*).

Green olive oils should be tested for **copper**, some specimens of "*Malaga* oil" being coloured green by admixture with copper acetate. Copper is best detected in the manner described above (Vol. I. Chap. IV.).

In the following lines I collate the most useful tests for the detection of those oils which occur as adulterants [1] in commercial olive oils :—

1. **Arachis Oil.**—Iodine absorption; as a rule, the amount of iodine absorbed will be higher than that of normal olive oil. *Determination of arachidic acid* (see "Arachis Oil," p. 252).

Tortelli's statement that an arachis oil free from arachidic acid can be prepared by subjecting arachis oil to a demargarinating process is not borne out by the author's experiments. Several samples of demargarinated arachis oil examined in the author's laboratory still contained considerable proportions of arachidic acid, sufficient to render the detection of an admixture of such arachis oil to olive oil easy.

Recently there have been brought into commerce olive oils, said to be genuine Tunisian oils, which yielded arachidic acid to the extent of 0·34 to 0·87 per cent. In order to ascertain definitely whether genuine Tunisian olive oils did contain so considerable an amount of arachidic acid, an examination was made of undoubtedly genuine Tunisian and also of Algerian oils obtained by the author and *Bontoux*.

These specimens were examined by *Archbutt* [2] with the result set out in the following table :—

[1] It may be pointed out that adulterated olive oils, especially olive oils for technical purposes, have again appeared in the market in considerable quantities. In Italy it has been found necessary for the protection of the olive oil industry to promulgate a law (in 1908) aiming at the repression of frauds in the olive oil trade.

[2] *Journ. Soc. Chem. Ind.* 1907, 453 ; 1185.

[TABLE

Tunisian and Algerian Oils from	Colour.	Specific Gravity at 60° F.	Free Acid (as Oleic Acid).	Saponification Value.	Iodine Value (Wijs).	Unsaponifiable Matter.
			Per cent.	Per cent.	Per cent.	Per cent.
1. Sousse, Tunis, 1906-1907 harvest. "Congealing."	...	0·9170	...	191·9	85·4	0·95
2. Sousse, Tunis, 1906-1907 harvest . .	Yellow	0·9175	...	191·6	86·2	0·81
3. Bône-Guelma, Algeria, 1906-1907 harvest .	Golden yellow	0·9167	...	191·7	83·2	0·89
4. Medjez-Amar, Algeria, Province of Constantine, 1906-1907 harvest. "Non-congealing."	Golden yellow	0·9173	...	190·3	90·5	0·97
5. Tunis. Variété Chétui, Mornag . .	Pale yellow (primrose)	0·9178	...	190·4	94·7	0·92
6. Tunis. Variété Chemlali, Sfax . . .	Yellow	0·9162	...	190·6	80·2	0·88
7. Tunis. Variété Chemlali, Gabès . .	Pale yellow (primrose)	0·9169	...	190·9	86·9	0·77
8. Tunis. Variété Chétui, Bizerte . . .	Yellow	0·9171	...	189·2	91·1	0·91
9. Tunis. Variété Besbassi, Rhadès-Tunis .	Brownish yellow	0·9164	...	190·4	82·7	1·15
Algerian Oils from						
1. Guelma, expressed from mixed olives . .	Pale grass green	0·9173	1·1	189·9	89·7	0·89
2. Guelma, expressed from the olives "Verdale" and "Roussette."	Pale greenish yellow	0·9169	4·5	189·6	90·4	0·81
3. Medjez-Amar from the olives "Roussette" and "Blanquette." 1st expression	Golden yellow	0·9169	0·9	189·6	89·0	0·88
4. Medjez-Amar from the olives "Roussette" and "Blanquette." 2nd expression	Brownish yellow	0·9171	0·9	189·2	89·8	0·96
5. Guelaat bou Sba from "Roussette" olives. 1905 crop	Primrose yellow	0·9173	0·4	190·1	90·1	0·80
6. Guelaat bou Sba from "Roussette" olives. 1906 crop	Pale primrose yellow	0·9178	0·5	189·2	90·3	0·72
7. Duvivier from the olives "Blanquette" and "Roussette."	Yellowish green	0·9178	2·3	189·0	88·5	0·78
8. Tlemcen	Golden yellow	0·9166	0·5	189·6	84·9	0·92
9. Mizrana, near Tizi Ouzou. From mixed olives, but especially "Chemlali" and "Aberkou" varieties.	Pale greenish yellow	0·9168	0·6	191·3	83·7	0·74
10. l'Oued Aissi, near Tizi Ouzou. From mixed olives.	Primrose yellow	0·9164	1·6	190·7	82·4	0·77
11. Mirabeau, near Tizi Ouzou. From mixed olives from the valley of l'Oued Bougdoura	Pale greenish yellow	0·9165	2·1	191·0	82·5	0·98
12. Makouda of the ordinary mixed olive oil of Mizrana.	Pale greenish yellow	0·9165	2·4	191·3	82·4	0·88

In Renard's arachidic acid test the following results were obtained:—Tunisian Oils, Nos. 1 and 2, gave some crystals at 15° C. No. 3 gave only a trace, and No. 4 none. After filtering and washing, the first crystals from No. 1 left 0·0123 gram of acids of melting point 55·6° C. On recrystallising these acids from 10 c.c. of 90 per cent alcohol, nothing separated after standing one hour at 15° C. In a second experiment with oil No. 1 only 0·0007 gram remained after washing the crystals which had separated at 15° C.

10 grams of oil No. 2 gave 0·001 gram fatty acid at 15° C. after washing. From 10 grams of the oils Nos. 5, 6, 7, 8, 9 no "arachidic acid" was obtained. On the first crystallisation of the acids, the lead salts of which are ether-insoluble, from 90 per cent alcohol at 15° C., small quantities of crystals were obtained from oils Nos. 5, 8, and 9, and a considerable quantity from Nos. 6 and 7. After filtering and washing with 90 per cent alcohol the following quantities of acids remained:—

No. 5	·0014 gram
No. 6	·0105 gram of melting point 56·7° C.
No. 7	·0018 gram
No. 8	·0102 gram of melting point 55·6° C.
No. 9	·0025 gram

On attempting to recrystallise the acids obtained from Nos. 6 and 8 from 5 c.c. of 90 per cent alcohol, nothing separated even after standing for more than an hour at 4° C.

From the last twelve samples no trace of arachidic nor lignoceric acid could be obtained. In contradistinction to the Tunisian oils, none of the fatty acids of Algerian oils separated from the ether-insoluble salts, yielded even traces of a crystalline precipitate when dissolved in 50 c.c. of 90 per cent alcohol, and cooled to 15° C.

From observations made recently by the author it appears that adulteration even of technical olive oil with arachis oil is on the increase.

2. **Sesamé Oil.**—Specific gravity; iodine absorption of the oil and of its liquid fatty acids; and, as most characteristic, *Baudouin's* test as modified by *Villavecchia* and *Fabris* (see "Sesamé Oil," p. 177). In order to avoid errors that might be caused by abnormal oils, such as Tunisian, etc., the liquid fatty acids should be examined. *Tortelli's* statement that sesamé oil can be freed from the chromogenetic substance, which can be detected by the *Baudouin* test, by filtering over charcoal, has not been borne out by experiments made by the author.

3. **Cotton Seed Oil.**—Specific gravity; melting point of fatty acids, iodine absorption of the oil, iodine value of the liquid fatty acids. Colour reactions as confirmatory tests (p. 162).

It should be borne in mind that some genuine olive oils give the *Becchi* reaction very distinctly (*Tortelli* and *Ruggeri*); in doubtful cases the liquid fatty acids should, therefore, be tested. It should further be remembered that if heated cotton seed oil has been used for adulteration, the *Halphen* and *Becchi* tests fail.

As an illustration of how far it is possible to detect adulteration by examining the liquid fatty acids, I have calculated the following table, in which the iodine values of the liquid fatty acids of the mixtures named are worked out for the lowest and highest values of olive and cotton seed oils respectively.

Olive Oil.	Cotton seed Oil.	Iodine Value of Liquid Fatty Acids.			
Per cent.	Per cent.	I.	II.	III.	IV.
100	0	95	95	104	104
95	5	97·6	97·8	106·15	106·35
90	10	100·2	100·6	108·3	108·7
85	15	102·8	103·4	110·45	111·05
80	20	105·4	106·2	112·6	113·4
0	100	147	151	147	151

It will be seen that by this test alone, small quantities of cotton seed oil cannot be detected; still more difficult is its detection if arachis oil be present.

4. **Rape Oil.**—Iodine absorption of the oil and of the liquid fatty acids; melting and solidifying points of the mixed fatty acids; *saponification value.* With regard to arachidic acid, cp. p. 205.

5. **Castor Oil.**—Specific gravity; *acetyl value*; (cp. also 10) behaviour with solvents.

6. **Curcas Oil** (used in Portugal, according to *Hiepe*, to adulterate olive oil).—Iodine absorption. Admixtures of even 10 per cent are said to be detected by the intense reddish-brown colouration the sample will assume a short time after treatment with nitric acid and metallic copper (in the elaïdin test).

7. **Lard Oil.**—Melting point of fatty acids; viscosity; odour of lard on warming. *Phytosteryl acetate test.*

8. **Drying Oils.**—Iodine value. Thermal tests. Bromide test.

9. **Fish Oils.**—The detection of fish oil in olive oil is required in the case of olive oil which is intended for preserving sardines, etc. (Since the body oil of the sardine becomes intermixed with the olive oil used for preserving the fish, fish oils will always be present to some extent in olive oil which has been drawn from the tins containing preserved fish.[1]) Fish oils are detected by the taste and smell, especially on warming, and notably by the high iodine value of the sample. In doubtful cases the isolation of insoluble brominated fatty acids must be resorted to. If required, the oil must be tested for the presence of metals dissolved from the tins.[2]

[1] Thus an olive oil of the iodine value 78·9, employed for preserving sardines, and taken from the tins after two months, one year, and two years, absorbed 99·02, 109·05, and 126·2 per cent of iodine respectively.—Klein, *Zeit. f. angew. Chemie*, 1900, 559. Similarly, an oil of the iodine value 84·9 used in the preservation of sprats and taken from the tins after one year, showed the iodine value 97·2.—Henseval and Deny, *Trav. de la Station Maritime à Ostende*, 1903.

[2] Cp. G. Salamone, *Giorn. Farm. Chim.* 55, 241.

10. **Grape Seed Oil**, stated by *Tortelli* to be used for the adulteration of olive oil, would be detected by a notable acetyl value of the sample; cp. also "5. Castor Oil."

11. **Maize Oil**, also stated by *Tortelli* to be used for adulterating olive oil, can be detected by the high iodine value of the sample and of its liquid fatty acids. It appears, however, very unlikely that maize oil would be used for the adulteration of the better class olive oils on account of its pronounced taste.

12. **Hydrocarbons.**—Determination of unsaponifiable matter. Adulterants falling under this class are: colourless vaseline and mineral oils.

When testing a suspected olive oil, it should be borne in mind that the adulterator has kept pace with the progress of our analytical methods, and that, in order to render detection more difficult, he no longer uses one single oil, but prefers a mixture of several oils. Thus, it has been pointed out by *Jean*[1] that olive oil is frequently adulterated with 8 to 10 per cent of a mixture consisting of equal parts of poppy seed, cotton seed, sesamé, and arachis oils. In a case of this kind, the determination of the iodine value of the liquid fatty acids will furnish the first and most important indication, after the presence of sesamé oil has been ascertained by means of the *Baudouin* test.

A method for the detection of sulphur olive oil in expressed olive oil has been based by *Halphen*[2] on the conversion of sulphur compounds into thiosulphates, which remain in solution when the soap is salted out by sodium sulphate. Fifty c.c. of the sample are saponified with 12 c.c. of a solution of 100 grams of pure sodium hydroxide in 75 c.c. of water, by heating to 110° C. in a basin. The heating is then continued until the mass ceases to froth, the temperature reaching then about 160° C. The mass is continually stirred until the temperature has fallen to 110° C. The finely granulated soap is dissolved in 200 c.c. of hot water, and the solution agitated until cold. The solution is then shaken with 100 c.c. of a saturated solution of sodium sulphate, after which 20 c.c. of a 33 per cent solution of copper sulphate are introduced, and the liquid thoroughly stirred and filtered. The object of adding the copper sulphate is to convert into soluble copper salts foreign substances occurring in certain expressed olive oils, which give a slight brown precipitate with silver nitrate. If the filtrate is not faintly green, it should be treated with an additional 0·2 c.c. of the copper sulphate solution and again filtered. To 100 c.c. of the clear filtrate there are then added 5 c.c. of a solution consisting of 1 part of a 5 per cent solution of silver nitrate, with 5 parts by volume of glacial acetic acid, and the whole gently heated to the boiling-point, then cooled, and rendered slightly alkaline with ammonia. In the presence of sulphur olive oil a brown or black precipitate will be observed.

[1] *Annal. de chim. anal.* 1898, 218. [2] *Journ. Pharm. Chim.*, 1905, xxi. 54-56.

The uses of olive oil have been incidentally mentioned in the foregoing pages. It need, therefore, only be briefly pointed out that the better qualities of olive oil are used in enormous quantities as an edible oil—the edible oil *par excellence*. Very large quantities of good edible oils are exported, chiefly from Bari, for the preservation of sardines, sprats, etc. Lower qualities are used in the industries as burning oils, lubricating oils, wool oils, and soap oils. The medicinal soaps are made chiefly from olive oil. Textile soaps of the highest quality for industrial purposes are also made from olive oil, such as soaps for degumming silk and for washing best woollen cloth. Soaps for the latter purpose are either hard or soft. Calico printers require, for the best class of goods, soaps made exclusively from olive oil. For the lowest textile soaps and for household soaps the highly acid bagassa oils and sulphur olive oils (yielding green olive soaps) are used. Such oils are largely used in the manufacture of mottled soaps in the south of Europe ("*Savon marbré de Marseille*").

The use of tournant oil has been mentioned already. The introduction of the sulphonated oils (Vol. III. Chap. XV.) has greatly reduced the consumption of the tournant olive oil.

OLIVE KERNEL OIL

French—*Huile de noyaux d'olive.* German—*Olivenkernöl.*
Italian—*Olio di noccioli d' oliva.*

For table of characteristics see p. 299.

Olive kernel oil is the oil obtained (by pressure or extraction) from the seeds contained in the olive stones. What had been formerly described as olive kernel oil was a highly rancid olive oil containing such quantities of olive kernel oil as would be expressed from the seeds on grinding the marc and crushed kernels with water (p. 281)[1] in the second and third expressions. It has been pointed out above (p. 280) at what stage of the process of producing olive oil the kernels are separated from the marc.

Olive kernel oil obtained by expression in the cold has a golden-yellow colour; the oil expressed in the hot possesses a greenish tint, whereas kernel oil extracted with solvents is dark green, no doubt owing to the presence of chlorophyll.

The taste of the expressed oil is sweetish, somewhat resembling that of almond oil, without, however, possessing the characteristic bland taste of olive oil.

The kernels constitute about 2·5 per cent of the weight of the entire fruit; they yield from 25 to 28 per cent of oil.

Olive kernel oil contains about 10 per cent of solid fatty acids, amongst which were identified stearic and palmitic acids, but not arachidic acid. The chief constituent of the liquid fatty acids is oleic acid; small quantities of linolic acid also occur in the oil.

[1] Klein, *Journ. Soc. Chem. Ind.* 1898, 1055.

The expressed oil in its fresh state is practically free from fatty acids. The oils expressed by *Klein* contained from 1·0 to 1·78 per cent of free fatty acids; the expressed mass, after drying, yielded to solvents an oil containing 30·4 per cent of free fatty acids, owing to decomposition of the glycerides during the prolonged contact of the oil with the organic matter.

The solubility of the oil in alcohol does not materially differ (in contradistinction to former statements) from that of olive oil.

In other respects also the oil closely resembles olive oil. Olive kernel oil naturally occurs in those olive oils which have been obtained from olive marc crushed with the kernels.

Klein proved by special experiments that the belief prevalent amongst olive growers, that the crushing of the kernels causes olive oil to turn rancid easily, is groundless. *Mingioli*[1] arrived at conclusions diametrically opposed to those of *Klein*, but *Marcille*[2] has shown that the latter's statements must be upheld. *Marcille* proved by experiments that the kernels contain an enzyme which acts on their non-fatty constituents (starch, sugar, glucosides), whilst exhibiting an extremely feeble lipolytic action. Hence the very short time during which, in ordinary practice, the broken kernels remain in contact with the pulp of the olive can have no deteriorating influence on the quality of the olive oil, prepared as described under "Olive Oil" (cp. footnotes, pp. 280, 281).

The press residue from olive kernels should yield, like that from other seeds, a good feeding cake; indeed, where the kernels are kept separate from the broken shells, the cakes obtained on pressing are used for feeding purposes. The broken shells are used as fuel. Proposals have been made frequently to work up these residues for the production of acids, methylalcohol, acetones, etc., by subjecting them (together with the exhausted olive marc residues) to a process of dry distillation.

Physical and Chemical Characteristics of Olive Kernel Oil

Oil obtained by	Specific Gravity.		Saponification Value.		Iodine Value.		Refractive Index.	
	At 15° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 25° C.	Observer.
Expression of fresh kernels	0·9184-0·9191	Klein	182·3-183·8	Klein	86·99-87·8	Klein	1·4682-1·4688	Klein
Drying and subsequent extraction of the pressed kernel	0·9193	,,	181·2	,,	87·1	,,	1·4673	,,

[1] *Bolletino della Società degli agricoltori italiani*, 1906.

[2] *Bulletin de la Direction de l'Agriculture du Commerce et de la Colonisation : Tunis*, 1907.

CALOPHYLLUM OIL

French—*Huile de Calophyllum.* German—*Kalophyllumöl.*
Italian—*Olio di Calophyllum.*

For tables of characteristics see p. 301.

Calophyllum oil is obtained from the nuts of *Calophyllum inophyllum*, L., a tree indigenous to tropical Asia and the coast of East Africa. The nuts described by *Hooper* are Indian nuts, and the oil is known in India under the name "Laurel Nut Oil," "Domba Oil," and "Alexandrian Laurel Oil" (see table facing p. 192). The oil is also known under the names "Poonseed Oil"; "Tacamahac Fat" (Réunion, Nossi-bé), from *C. Tacamahaca*; "Njamplung Oil"; Calaba Oil (Martinique and Guadeloupe), from *C. Calaba.*

In the examination of a large consignment of nuts of *Calophyllum inophyllum* the author[1] found them to consist of 62·9 per cent of shells and mesocarp and of 37·1 per cent of kernels. The latter yielded by expression in the hot (in a hydraulic press) 35·6 per cent of oil.

The specimen of oil examined by *Fendler*[2] was obtained from *Calophyllum* nuts, from the island Yap (Jap, Carolines). The kernels yielded from 50·5 to 55 per cent of oil containing about 15 per cent of a green resin, which can be extracted by treatment with a solution of sodium carbonate. The characteristics obtained for the oil, containing 15 per cent of the resin, of the neutralisation value 198, are given in the table (p. 301). This crude oil had the acid value 28·45, and yielded 0·25 per cent of unsaponifiable matter. In the *Livache* test the oil absorbed after 18 hours 0·25 per cent oxygen, and after 136 hours 1·84 per cent.

The characteristics obtained from the oil, after freeing it from the resin, are given in the table (p. 301).

The oil consists of the glycerides of palmitic, stearic, and oleic acids.

The natives use the oil for medicinal and illuminating purposes. Owing to the poisonous properties of the oil, and especially of the resin contained in the crude oil, it cannot be used as an edible oil.

[1] Unpublished observations.

[2] *Apotheker Ztg.* 1905, No. 1.

[TABLE

Physical and Chemical Characteristics of Calophyllum Oil

	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
	At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Butyro-refractometer. "Degrees."	
														At 40° C.	Observer.
	16	0·9315	Hooper[1]					196·4	Hooper						
Oil containing resin	25	0·9428	Fendler	+3	Fendler	+8 separates "stearine" on standing.	Fendler	196·0	Fendler	92·8	Fendler	0·13	Fendler	76	Fendler
Oil freed from resin								191·0	,,	86·0	,,	0·18	,,		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
33	Fendler	38	Fendler	194	Fendler	289·2	Fendler	92·2	Fendler
				Liquid Fatty Acids.		Liquid Fatty Acids.		Liquid Fatty Acids.	
				190·7	Fendler	294·2	Fendler	114·5	Fendler

[1] *Pharm. Journ. Trans.* 1889 (10), 525 ; cp. also *Journ. Soc. Chem. Ind.* 1901, 642.

COFFEE BERRY OIL

French—*Huile de café.* German—*Kaffeebohnenöl.*
Italian—*Olio di caffè.*

For tables of characteristics see pp. 303, 304.

Coffee berry oil—extracted with solvents from coffee berries (*Coffea arabica*, L.)—has an intense greenish-brown colour; it possesses a faint odour of raw coffee. By roasting the berries the oil is very little changed. According to *Hilger* and *Juckenack*,[1] the loss of oil during the roasting of coffee berries amounts to 9 to 10 per cent; berries glazed with sugar lose about 20 per cent. Java berries yielded on extraction with petroleum ether 9 per cent of oil (*Warnier*[2]).

The samples examined by *Spaeth* contained from 2·25-2·29 per cent of free fatty acids, calculated as oleic acid.

According to *Hilger*, coffee berry oil consists of olein and small quantities of palmitin and stearin.[3]

[1] *Analyst*, 1897, 287. [2] *Pharm. Weekblad*, 44 (1907), 1080.
[3] *Chem. Zeit.* 1895, 776 (Hehner and Mitchell's method was not known then).

Physical and Chemical Characteristics of Coffee Berry Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·9510-0·9525	De Negri and Fabris[1]	5 – 3 6 – 3	De Negri and Fabris			165·1-173·37	De Negri and Fabris
							176·2-177·3	Spaeth[2]
24·5	0·942	Warnier[3]	5-6	Warnier	8·9	Warnier[3]	177·5	Warnier[3]

Physical and Chemical Characteristics of Coffee Berry Oil—continued

Reichert-Meissl Value.		Iodine Value.		Maumené Test.	Refractive Index.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	At 25° C.	Observer.
1·65-1·7	Spaeth	85·89-87·34 (78·65)	De Negri and Fabris	53-55[1]	1·4777-1·4778	Spaeth
					Butyro-refractometer. "Degrees." At 25° C.	
		85·3-86·8	Spaeth			
		85	Warnier[3]		79-79·25	Spaeth
					81·5	Warnier

[1] De Negri and Fabris, *Anali del Labor. chim. delle Gabelle*, 1893, 253.

[2] Spaeth, *Chem. Zeit.* 1895, Rep. 292.

[3] From Java beans.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.
°C.	°C.	Mgrms. KOH.	Per cent.
36 – 34	38-40	172-178	88·82-90·35
...	...	...	(81·8)

UNGNADIA OIL[1]

French—*Huile d'ungnadia.* German—*Ungnadiaöl.*
Italian—*Olio di ungnadia.*

Ungnadia oil is obtained from the seeds of *Ungnadia speciosa*, Endl., a tree indigenous to Texas.

Physical and Chemical Characteristics of Ungnadia Oil

Specific Gravity.		Solidifying Point.	Saponification Value.	Iodine Value.
At °C.		°C.	Mgrms. KOH.	Per cent.
15	0·9120	– 12	191-192	81·5-82
100	0·8540			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Solidifying Point.	Melting Point.	Iodine Value.
Per cent.	°C.	°C.	Per cent.
94·12	10	19	86-87

BEN OIL

French—*Huile de ben.* German—*Behenöl.*
Italian—*Olio di ben.*

For tables of characteristics see p. 306.

Ben oil is prepared from the seeds of the ben nut from *Moringa pterygosperma*, syn. *oleifera*, and *Moringa aptera*, Gärt.[2] The Moringa

[1] Schaedler, *Pharm. Zeitung*, 1889, 340. [2] *Bull. Imp. Inst.* 1904, 117.

trees are indigenous to India, Arabia, and Syria, and were introduced into Jamaica from the East Indies in the year 1784.[1] Latterly, *Moringa pterygosperma* has been found in Northern Nigeria, and in Dahomey.

The Jamaica seeds consist of 40 per cent of husks and 60 per cent of kernels. Genuine ben oil received at the Imperial Institute from Jamaica gave, on filtering at 17° C., 60 per cent of liquid material, and 40 per cent of a nearly white solid fat. A specimen of the latter obtained by the author[2] from the Imperial Institute represents at the ordinary temperature a whitish or yellowish-white translucent mass melting at about 25° C. Other specimens described in the table of characteristics are liquid at the ordinary temperature, and some "stearine" separates from them on standing at about 0° C.

Northern Nigerian seeds submitted to the author by the Imperial Institute contained 33·27 per cent of oil. The seeds consisted of 8 per cent of husks (forming a light coloured skin), and 92 per cent of kernels, so that the shelled kernels would yield 36·16 per cent of ben oil; on the average 552 seeds weigh 100 grams.

These seeds were expressed in two stages on a semi-large scale, and yielded a cold-pressed oil and a hot-pressed oil. The examination of these two oils in the author's laboratory gave the following numbers :—

	Cold-pressed crude Ben Oil.	Hot-pressed crude Ben Oil.
Specific gravity at 40° C. water at 40° = 1	0·9018	0·8984
Acid value	49·71	100·5
Saponification value	179·2	178·7
Unsaponifiable matter	1·67 per cent	2·69 per cent
Iodine value	100·3	88
Titer test of the fatty acids	32° C.	38·2° C.

Refined ben oil has a slightly yellowish colour, is odourless, and has a sweet taste.

Ben oil is stated to consist of the glycerides of oleic, palmitic, and stearic acids, and of a solid acid of high melting point; according to *Völcker*,[3] this acid is identical with behenic acid, melting point 76° C. [arachidic acid?]. The phytosterol isolated from ben oil by *L. van Itallie*[4] and *C. H. Nieuwland* had the melting point 131-135° C.

In the East ben oil serves as a cosmetic; it used to be employed in the "maceration" process for extracting perfumes from flowers.

[1] *Bulletin*, Imperial Institute, 1904, 117.
[2] Lewkowitsch, *Analyst*, 1903, 343. [3] Liebig's *Annalen*, 64, 342.
[4] *Archiv d. Pharm.* 244 (1906), 159.

Physical and Chemical Characteristics of Ben Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	"Degrees."	Observer.
15	0·9120	Chateau	Solidifies	Chateau	185·6 [5]	Lewkowitsch	84·1 [1,2]	Mills	40	60·5 [4]	Lewkowitsch
,,	0·9198 [2]	Mills	completely		186·17-	,,	80·8 [1,3]	,,	,,	59·0 [5]	,,
,,	0·9161 [3]	,,	at 0;		187·7 [6]		111·8 [4]	Lewkowitsch	,,	50·0 [6]	,,
15·5	0·91998 [4]	Lewkowitsch	deposits		184·6 [4]	,,	109·9 [5]	,,	,,	59·0 [7]	,,
,,	0·91840 [5]	,,	crystals				72·2 [6]	,,			
,,	0·91267 [6]	,,	at 7				112·6 [7]	,,			
			8·8 [6]	Lewkowitsch							

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	
°C. Titer Test.	Observer.
37·2-37·8	Lewkowitsch

[1] Calculated from bromine value. [2] Containing much solid fat. [3] Containing no solid fat. [4] Freed from "Stearine."
[5] Portion solid at 0°. [6] Oil from *Moringa pterygosperma*. [7] Commercial oil.

On the strength of experiments made in Kingston, Jamaica, in 1817, ben oil was considered an exceedingly valuable oil for delicate machinery, and was credited with the property of not easily turning rancid. This statement has hitherto been copied from text-book to text-book, and ben oil was looked upon (just like cacao butter) as an oil which does not become rancid. From the above-given notes (supported by experiments made in the author's laboratory with refined oil) the statement must now be looked upon as erroneous. Ben oil becomes rancid just like any other oil having the same consistence and composition, the state of rancidity of a given specimen depending on the manner in which it has been kept. The oil if properly refined would yield a good edible oil, and, if properly kept, should be a valuable lubricating oil for delicate machinery.

STROPHANTUS SEED OIL[1]

French—*Huile de strophante.* German—*Strophantusöl.*
Italian—*Olio di strofanto.*

Physical and Chemical Characteristics of Strophantus Seed Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
13	0·9254	Mjöen[1]					187·9	Mjöen
15½	0·9249	Bjalo-brzewski[2]	−6	Bjalo-brzewski	+2	Bjalo-brzewski	194·6	Bjalo-brzewski

Physical and Chemical Characteristics of Strophantus Seed Oil—continued

Iodine Value.		Reichert-Meissl Value.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
73·02	Mjöen	0·5	Mjöen
101·6	Bjalo-brzewski	0·9	Bjalo-brzewski

This oil is obtained from the seeds of *Strophantus hispidus*, which contain 22 per cent of oil. The oil has a brownish-green colour, appearing yellowish-brown by transmitted light.

[1] Mjöen, *Archiv d. Pharmacie*, 1894 (234), 283.
[2] *Journ. Soc. Chem. Ind.* 1901, 817.

The sample examined by *Bjalobrzewski* contained 12 per cent of free fatty acids, and traces of a volatile oil. Amongst the volatile acids formic acid was identified; from the insoluble fatty acids oleic, stearic, and arachidic acids were isolated (by fractional distillation of the ethylic esters).

The melting point of the insoluble fatty acids was 28°-30° C.

SENEGA ROOT OIL

French—*Huile de Polygala de Virginie.* German—*Senegawurzelöl.* Italian—*Olio di Senega.*

This oil is obtained from the roots of *Polygala Senega*,[1] L., from which 4·55 per cent of oil can be extracted. The oil is readily soluble in the usual solvents; it dissolves with difficulty in xylene, and is only partially soluble in petroleum ether.

The acid value of the oil was 37·9, and its acetyl value 34·46. The specimen examined by *Schroeder* contained 12·8 per cent of unsaponifiable matter; this consisted chiefly of resinous substances, insoluble in petroleum spirit. The volatile fatty acids are stated to contain valeric acid, and also salicylic acid.

The unsaturated fatty acids had the iodine value 82·4. The saturated fatty acids had the melting point 61° C. *after* repeated recrystallisation; their mean molecular weight was found to be 260. The composition of the Senega root oil is given by *Schroeder* as follows:—unsaponifiable matter, 12·78 per cent; palmitin, 7·9 per cent; olein, 79·3 per cent.

Physical and Chemical Characteristics of Senega Root Oil

Specific Gravity.		Saponification Value.	Iodine Value.	Reichert-Wollny Value.	Insoluble Acids + Unsaponifiable.
At ° C.		Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.
18	0·9616	193·8	81·8[2] 78·4[3]	6·43	85·8

[1] A. Schroeder, *Archiv d. Pharmacie*, 1906 (243), p. 638, and *Journ. Soc. Chem. Ind.* 1906, 128.

[2] Oil containing the unsaponifiable matter.

[3] Oil free from the unsaponifiable matter.

STERCULIA OIL—OIL OF JAVA OLIVES [1]

French—*Huile de Sterculia; huile de l'olive de Java.* German—*Sterculiaöl (Java Olivenöl).* Italian—*Olio di Sterculia; olio d' oliva di Java.*

For tables of characteristics see p. 310.

This oil is obtained from the seeds of *Sterculia foetida*, L., a tree widely distributed over the Dutch Indies, Indo-China, the East Indies, and the Malayan Archipelago. It is cultivated in these countries, as also in Guayana (Cayenne), on account of its wood (which in its green state has an unpleasant smell, and is therefore termed in the trade "bois puant," stinking wood). The seeds are known in commerce under the name "Olives of Java," "Kaloempang beans," "Beligno seeds," or "Sterculia kernels."

The average weight of the seeds is 2·4 grms. They are formed of an outer parchment-like skin of violet or blackish colour which can be easily removed. Below the skin is found a dark fleshy mass — pulp — which adheres to the husk of the kernel. The latter consists of a whitish endosperm having a pleasant taste.

Wedemeyer [2] obtained from the skin and pulp by extraction (the nature of the solvent is not stated) 9·8 per cent of a yellow buttery fat, and from the kernels 46·6 per cent of a liquid, light yellow oil. The whole seeds yielded 30·3 per cent of a liquid, light yellow oil. *Greshoff* [3] obtained 58·65 per cent of oil from the dry seeds, which originally contained 7·8 per cent of water. The characteristics placed in the tables against *Wedemeyer* refer to the oil obtained from the whole seeds by expression. This expressed oil is of a pale yellowish colour. The specimen prepared by *Wedemeyer* contained 2·6 per cent of free fatty acids, and 1·7 per cent of unsaponifiable matter. The acetyl value of the mixed fatty acids (determined by *Benedikt* and *Ulzer's* faulty method) was 23·5.

Bontoux [4] examined separately the oils obtained from the pulp and kernels of seeds which furnished 17 per cent of skin and pulp, 30 per cent of husks, and 53 per cent of kernels. The skin and pulp yielded 28·6 per cent and the kernels 53·6 per cent of oil respectively by extraction with carbon bisulphide. The fatty matter obtained from the former was a pasty mass of a light yellow colour, which becomes perfectly clear on warming above 30° C. The expressed fat has a pleasant odour and taste.

[1] Since the name "Java Olives" appears misleading, I prefer to name this oil "Sterculia Oil."

[2] *Zeit. f. Unters. Nahrungs- u. Genuss.* 1906, xii. p. 210.

[3] *Chem. Zeit.* 1906, 856.

[4] Lewkowitsch, *Technologie et Analyse chimiques des Huiles, Graisses et Cires, traduit par E. Bontoux*, vol. ii. p. 902.

Physical and Chemical Characteristics of Sterculia Oil

	Specific Gravity.		Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Maumené Test.	Refractive Index.	Observer.
	At ° C.		Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	° C.	At 40 ° C.	
Pulp oil . . .	...	...	172·4 [1]	81·4 [1]	...	...	...	Bontoux
			192·8 [2]	58·7 [2]	...	...	...	,,
			193·8 [3]	56·5 [3]	...	...	...	,,
Kernel oil . .	...	...	173·4 [2]	81·4 [2]	...	...	...	,,
			174·3 [3]	83·1 [3]	...	...	...	,,
Whole oil . .	15	0·9260	187·9	76·6	0·8	158	1·4654	Wedemeyer [4]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Fatty Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Neutralisation Value.	Saponification Value.	Iodine Value.	Observer.
	Per cent.	° C.	° C.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	
Pulp oil . . .	95·7	43 (Titer)	46·5	199·2	203·8	57·7	Bontoux [3]
Kernel oil . .	95·4	viscous thickening at 25-27	...	85·6 [5]-98·7 [6]	190·8 [5]-186·8 [6]	...	...
Whole oil . .	95·6	...	...	...	...	...	Wedemeyer

[1] Expressed oil. [2] Extracted by petroleum ether. [3] Extracted by carbon bisulphide.
[4] Expressed oil from the whole seeds.
[5] Means of five determinations with fatty acids of different preparations, dried at 110-115° C.
[6] Means of five determinations with fatty acids of different preparations, dried at 40° C. *in vacuo*.

The extracted *kernel oil* is liquid, but slightly viscous; the expressed oil has a somewhat insipid taste and odour, recalling that of earth. Oil obtained by expression or by extraction with petroleum ether has a clear yellow colour, whereas oil extracted with carbon bisulphide exhibits a fine cherry-red colour. This colouration must be due to the action of traces of sulphur which are retained by the solvent, for in the *Halphen* test both the expressed oil as also that extracted with petroleum ether give a very intense cherry-red colour.

The oil obtained by extraction or by expression from the *whole seed* is liquid and slightly viscous. It has the same colour, taste, and odour as the *kernel oil* (of which it contains more than 85 per cent), but on standing some "stearine" separates at the ordinary temperature. The characteristics of the pulp oil and of the *kernel oil* are given separately in the tables.

The most characteristic property of the kernel oil, which is shared by the whole oil but not by the pulp oil (*Bontoux*), is its behaviour (first observed by *Wedemeyer*) on heating to 240°-245° C., when it is suddenly converted, with spontaneous generation of heat, into an indiarubber-like solid substance. If a somewhat large quantity of the oil be heated, say 1 kilo, the spontaneous generation of heat, if not prevented by cooling, causes the oil to ignite and become carbonised throughout its whole mass. If the oil be heated for a short time to 240° C. and the temperature be not allowed to rise above 250° C., a tough indiarubber-like substance is obtained, which remains elastic on exposure to the air, and is insoluble in the usual solvents. No doubt this property is due to a process of polymerisation. Having regard to the low iodine value of the oil, the process of polymerisation would appear to be similar to that of castor oil. It cannot, however, be caused exclusively, as in the case of castor oil, by hydroxylated fatty acids, as the acetyl value of the fatty acids from the kernel oil, determined by the author's method, was only 18·8 (*Bontoux*). The extraordinary rise of temperature in the *Maumené* test (see table of characteristics) would seem to offer some clue as to the characteristic behaviour of the oil on heating, and it seems, therefore, most likely that some new fatty acids are contained in sterculia oil, an indication of which is also given by variation of the saponification and iodine numbers (see tables of characteristics), and by the exceptionally low neutralisation value of the insoluble fatty acids.

In the polarimeter (*Soleil-Ventzke*, in a 200-mm. tube), very slight rotation was noticeable. The viscosity in *Engler's* viscosimeter was 6·52 at 20° C.

In Java the oil is used by the natives for culinary purposes, and also as a burning oil.

TROPÆOLUM OIL [1]

French—*Huile de cresson d'Inde.* German—*Tropäolumöl. Kapuzinerkressenöl.* Italian—*Olio di tropeolo.*

This oil is obtained from the seeds of *Tropæolum majus*, L.; it is a buttery mass, melting at a temperature slightly above the ordinary.

On standing, a very considerable portion crystallises from the oil; the crystals consist of pure trierucin.

The iodine value of tropæolum oil is 73·75; since this value differs but slightly from the theoretical number of trierucin—72·2—the oil may be considered as consisting chiefly of trierucin.

PARADISE NUT OIL [2]

French—*Huile de noix de paradis.* German—*Paradieskörneröl.* Italian—*Olio di noci del paradiso.*

For tables of characteristics see p. 313.

This oil is obtained from the seeds of *Lecythis Zabucajo*, Aubl. (*Quatelé Zabucajo*), a large tree belonging to the *Myrtaceæ*, and indigenous to Guiana and Brazil. The seeds contain from 50 to 51 per cent of oil.

The characteristics given in the table were determined by *De Negri* with an oil obtained from the Sapucaja nuts by extraction with petroleum ether. The oil was slightly yellow, odourless, and had an insipid taste; its acid value was 3·19. It was insoluble in cold glacial acetic acid, but dissolved in an equal volume of the hot acid. *De Negri* gives the acetyl value of 44·08 for the specimen examined by him; it is, however, doubtful whether the acetyl value is in this case a characteristic (due to the presence of a hydroxylated acid) or a variable, notwithstanding the fact that the amount of diglyceride and monoglyceride must have been small.

[1] Gadamer, *Arch. d. Pharmacie*, 1899, 273, 472.
[2] De Negri, *Journ. Soc. Chem. Ind.* 1898, 1156.

Physical and Chemical Characteristics of Paradise Nut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Refractive Index. Butyro-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer:	Per cent.	Observer.	At 15° C.	Observer.
0·895 (?)	De Negri	4	De Negri	173·6	De Negri	71·64	De Negri	61·3-61·5	De Negri

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
28·5	De Negri	37·6	De Negri	72·3	De Negri

SECALE OIL [1]

French—*Huile de seigle ergoté.* German—*Mutterkornöl.*
Italian—*Olio di segala cornuta.*

Secale oil is obtained from *Secale cornutum* (see Appendix).

Mjöen states that the oil has the acetyl value 62·9. The specimen examined by *Mjöen* yielded 96·3 per cent of fatty acids + unsaponifiable. The melting point of the insoluble fatty acids was 39·5°-42° C.

Physical and Chemical Characteristics of Secale Oil

Specific Gravity at 13° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9254	178·4	71·08	0·20

CANARI OIL [2]

French—*Huile de Canari.* German—*Canariöl.*
Italian—*Olio di Canari.*

For tables of characteristics see p. 315.

This oil, known under the trivial name Java almond oil, is obtained from the seeds of *Canarium commune*, L. (*Bursera paniculata Lam* = *Colophonia mauritania*, D. C.). The tree is indigenous to the Moluccas and Malabar; it is cultivated in tropical Asia, where the seeds serve as a foodstuff in place of sweet almonds, which they resemble in shape and taste. One thousand air-dried seeds weigh 5934·3 grms., yielding 809·8 grms. (13·64 per cent) kernels. One thousand kernels weigh 520 grms.

The seeds yield on extraction with solvents 65·7-68·6 per cent of oil; the extracted meal contains 34·7 per cent of proteids. On pressing the seeds, 56·1 per cent of oil was obtained.[3] The oil extracted from the kernels has a pale yellow colour and a pleasant, mild taste. At 15° C. "stearine" commences to separate. The unsaponifiable matter in the oil amounts to 0·44 per cent. The acid value of the specimen examined by *Wedemeyer* was 22·8, and the acetyl value 8·4; the acid value of the sample examined by *Pastrovich* was 1·3 for extracted oil,

[1] Mjöen, *Archiv d. Pharm.* 1894 (234), 278.
[2] Wedemeyer, *Seifensieder Zeitung*, 1907, 26.
[3] Pastrovich, *Chem. Zeit.* 1907, 782.

Physical and Chemical Characteristics of Canari Oil

Specific Gravity.			Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index. Butyro-refractometer at 40° C.	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	"Degrees."	Observer.
40 (water at 40=1)	0·8953	Wedemeyer	18-28·5	Pastrovich	193·5	Wedemeyer	64·7	Wedemeyer	0·1	Wedemeyer	59	Wedemeyer	49·5	Wedemeyer
	0·9050	Pastrovich			194·3	Pastrovich	65·6	Pastrovich	0·0	Pastrovich			51·2	Pastrovich

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point in Capillary Tube (Titer Test).		Melting Point of the Insoluble Fatty Acids (in Capillary Tube).		Neutralisation Value.		Saponification Value.		Mean Molecular Weight, from Neutral. Value.		Iodine Value.		Refractive Index. Butyro-refractometer at 40° C.	
Per cent.	Observer.	°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.		Observer.		Observer.	Per cent.	Observer.		Observer.
95·5	Wedemeyer	50 (water at 50=1	0·8825	Pastrovich	37·2	Wedemeyer	40·4	Wedemeyer	191·1	Wedemeyer	205·1	Pastrovich	278·6	Pastrovich	67·2	Pastrovich	35·7	Pastrovich
95·5	Pastrovich				41·0	Pastrovitch			201·6	Pastrovich					Liquid Fatty Acids.			
															110·4	Pastrovich		

and 0·84 for expressed oil, whilst the acetyl value determined with the fatty acids was 16·39 for the extracted, and 15·68 for the expressed oil. These acetyl values must not, however, be taken as undoubtedly indicating the presence of a hydroxylated acid. For in the former case the high acid value would rather seem to point to the presence of mono- and di-glycerides, and in the case of the determinations carried out by *Pastrovich* a faulty method had been used (cp. Vol. I. Chap. VI.). Moreover, the acetyl values found by the two observers differ considerably.

On separating the insoluble fatty acids by means of the lead-salt-ether method, *Pastrovich* obtained 44·6 per cent of solid fatty acids having the melting point 54·45° C., and the mean molecular weight 266. On precipitating fractionally the magnesium salts of the solid acids, stearic and palmitic acids were identified. On oxidising the liquid fatty acids (55·4 per cent), considerable quantities of dihydroxy-stearic acid and small quantities of sativic acid were obtained. No hexabromides were found; hence linolenic acid appears to be absent. The fatty acids of this oil consist, therefore, approximately, of 44·6 per cent of palmitic + stearic acids,[1] 43 per cent of oleic acid, and 12·5 per cent of linolic acid.

Castor Oil Group

In this group I comprise grape seed oil and castor oil. These two oils (pending further confirmation as regards grape seed oil) are remarkable for their high proportion of glycerides of hydroxylated fatty acids, as indicated by their high acetyl values. Owing to this composition castor oil is miscible with alcohol. This property is not shared by grape seed oil; for this reason it is doubtful whether grape seed oil is related to castor oil. This doubt is further increased by the circumstance that the grape seed oils described by the several observers differ greatly (see below).

GRAPE SEED OIL

French—*Huile de pépins de raisin.* German—*Traubenkernöl.*
Italian—*Olio di vinacciuoli.*

For tables of characteristics see p. 318.

Grape seed oil is obtained from grape seeds (from *Vitis vinifera*, L.) by expression or by extraction. The freshly expressed grape yields 25 per cent of seeds containing 6-20 per cent of oil. To obtain it,

[1] Oudemans, *Journ. f. prakt. Chemie* 81 (1860), 356; 99 (1866), 409, states that myristic acid occurs in this oil.

the seeds are dried by exposure to the air, ground subsequently to a coarse meal, intermixed with about 25 per cent of water, and expressed first in the cold and then in the hot. The quantity of oil in the seeds depends on the kind of grapes and the climate in which they are grown. According to some writers the seeds from white grapes are richer in oil than those from black, and sweet grapes yield more oil than those containing little sugar. Other writers state that the black grapes grown in warm countries are richer in oil (containing 10 to 20 per cent) of better quality. Whereas the average of grape seed oil recovered in some French mills was 8 per cent to 10 per cent, in Wurtemberg 10 per cent to 11 per cent of crude oil are generally obtained. The seeds contain the largest amount of oil at the time of vintage; on storing the seeds the quantity of oil decreases considerably.

The oil obtained by cold expression has a golden-yellow colour, and is free from odour. Oil from stored seeds is darker and has a slightly bitter flavour. Oil of the second expression is brown and has a bitter taste. Grape seed oil extracted by means of solvents is dark; it is stated to be obtainable as a perfectly colourless oil by filtering over animal char. The numbers recorded in the table refer to extracted oil. The oil dissolves easily in glacial acetic acid at 70° C.; the solution becomes turbid at 66·5° C. In 96 per cent alcohol it dissolves only partially.

Grape seed oil does not dry on exposure to air, or only after a long time (*De Negri* and *Fabris*).

The specimens of oil examined by various observers differ considerably. The iodine values of the two oils examined on the one hand by *Horn*, and by *De Negri* and *Fabris* on the other, agree tolerably well, and would point to similar oils. Very different from these oils are the grape seed oils examined by *Ulzer* and *Zumpfe* and by *Fabris* and *Settimj*[1] (see below).

The most prominent characteristic of grape seed oil is, according to *Horn*, its very high *acetyl value*, placing it, in this respect, in close relationship to castor oil. Since this number was obtained by *Benedikt* and *Ulzer's* method, it stands in need of confirmation. The high specific gravity stated by *Horn*, in conjunction with the low saponification value, would seem to confirm the high proportion of hydroxy acids. Yet, the specific gravity ascertained by *De Negri* and *Fabris*, and its immiscibility with alcohol, negatives a high proportion of hydroxy acids. The low saponification number found by *De Negri* and *Fabris* (practically identical with that stated by *Horn*) speaks, however, in favour of *Fitz's* statement,[2] that grape seed oil contains considerable quantities of erucic acid. This was isolated from the ether-soluble lead salts as a solid acid of the melting point 33° C., yielding, on fusion with caustic potash, a considerable amount of arachidic acid. The sample examined by *Horn* had the acid value 16·2.

[1] *Atti del VI. Congresso, etc.*, Roma, 1907, v. 762.
[2] *Berichte*, 1871, 442.

Physical and Chemical Characteristics of Grape Seed Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Acetyl Value.		Refractive Index.		
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.		Observer.	At °C.		Observer.
0·926	Jobst	−11	Jobst	178·4	Horn	94	Horn	0·46	Horn	52-54	De Negri and Fabris	144·5[1]	Horn	25	1·4713	Ulzer and Zumpfe
0·9202	Hollandt	−15	Hollandt	178·5-179	De Negri and Fabris	95·8-96·2	De Negri and Fabris	1·9	F. and S.			43·7	Ulzer and Zumpfe			
0·9561	Horn	to								64·5	F. and S.			50	1·4623	,,
0·935	De Negri[2] and Fabris	−17	De Negri and Fabris	190	U. and Z.	142·8	U. and Z.			81-83	U. and Z.	30·9	F. and S.			
		−10		178·3	F. and S.	130·3	F. and S.							Butyro-refractometer. "Degrees."		
0·9215	U. and Z.	to														
0·925	F. and S.	−13	F. and S.											25	68·5	U. and Z.
															70·3	F. and S.
														50	54·5	U. and Z.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
92·13	Horn	20-18	De Negri and Fabris	23-25	De Negri and Fabris	187·4	Horn	98·65	Horn
97·6 (!)	F. and S.							98·9-99·05	De Negri and Fabris
		20	F. and S.	25-26	F. and S.			132·5	F. and S.
								Liquid Fatty Acids.	
								151·7	F. and S.

[1] This value requires confirmation, having been determined by *Benedikt* and *Ulzer's* method.

[2] *Annali del Labor. chimico centr. delle Gabelle*, 1893, 225.

The very high iodine value which *Ulzer* and *Zumpfe*[1] have recorded for a specimen of grape seed oil would lead to placing it amongst the drying oils. An examination of the oil by the lead-salt-ether method, and the subsequent examination of the liquid fatty acids by *Hazura's* method, showed that this grape seed oil contained 7 to 8 per cent of solid fatty acids (calculated on the total fatty acids).[2] These consist most likely of stearic and palmitic acids (their mean molecular weight having been found 271, their m.p. 56° C., and their iodine value 0·4). Arachidic and lignoceric acids could not be found in *Renard's* test. Nor could erucic acid be obtained; hence its presence is extremely doubtful. On oxidising these fatty acids (the lead salts were easily soluble in cold ether) with potassium permanganate in alkaline solution in the cold, *Ulzer* and *Zumpfe* obtained: dihydroxystearic acid, considerable quantities of sativic acid, and probably also linusic acid. They state that also tri-hydroxystearic acid occurred amongst the products of oxidation. Final proof, however, has not been adduced to show that the supposed tri-hydroxystearic acid, of the m.p. 139° C. and mol. weight 333·9, did not consist of a mixture of other acids. The acetyl value of 43·7 found by *Ulzer* and *Zumpfe* cannot be taken, without further proof, as a confirmation of the existence of hydroxylated fatty acids in this grape seed oil, since the acetyl value was determined by a faulty method. In some small measure this is confirmed by the ready solubility in petroleum ether of the specimen examined by them. The same stricture would apply to the acetyl value given by *Fabris* and *Settimj*.

The conflicting statements as to its composition render the re-examination of grape seed oil desirable. Since this oil is not produced on a large scale, and is merely used up locally, it would be required to examine oils from different sources in order to clear up the differences pointed out above.

The oil of first expression is used locally—in France, in Wurtemberg, and in Italy as an edible oil. The hot-pressed oil (after refining with concentrated sulphuric acid) is used as a burning oil, and might even find an outlet for soap-making if it were produced in sufficiently large quantities. It has also been stated that grape seed oil is used in Italy for adulterating rape seed oil, and even olive oil, but conclusive proof for this assertion is wanting.

On the strength of the exceedingly high acetyl value which *Horn*[3] found, he proposed the employment of this oil as a substitute for castor oil in the manufacture of Turkey-red oil.

The press-cakes obtained in the preparation of the oil are used for feeding sheep and cattle. At the beginning of last century the cakes are stated to have been used by the poorer classes in Italy for the preparation of a tea-like beverage.

[1] *Oesterr. Chem. Zeitung*, 1905, 121.
[2] Fabris and Settimj obtained 15 per cent of solid fatty acids.
[3] *Mitth. des k.-k. technolog. Gewerbe-Museums*, 1891, 185.

CASTOR OIL

French—*Huile de ricin.* German—*Ricinusöl.*
Italian—*Olio di ricino.*

For tables of characteristics see pp. 327-329.

Castor oil is obtained from the seeds of *Ricinus communis*, L.

The origin of the name castor oil is due to the Spaniards and Portuguese in Jamaica having confounded the plant with a totally different one, viz. *Vitex agnus castus*, and having called it "agnocasto." The English traders corrupted this name into "castor" in the eighteenth century (cp. De Candolle's *Origin of Cultivated Plants*).

The plant seems to have been indigenous to Africa, but has been transplanted to India at a very early stage of history. In fact, some writers consider it to be indigenous to India itself. The plant is found in enormous quantities in all tropical and sub-tropical countries, and even growing wild to-day in South America, notably in Paraguay and Argentina. There is, therefore, an abundance of castor seeds to be obtained whenever the demand of the market increases. At present castor seeds are also collected in Southern Nigeria, and in the Italian colony Erythrea.

There are a number of varieties cultivated in India. In Bengal alone three distinct varieties of the plant are known. The first variety, growing to a height of about twelve feet, yields small, bright black seeds, dotted all over with grey. The second variety, requiring more care in cultivation, grows to a height of about six feet, and yields somewhat larger wheat-coloured seeds. The third variety, grown along with Indian corn, furnishes the largest seeds, which are slightly flattened, of a red colour and mottled.

In French Indo-China, where a large variety of the *Ricinus* plant is known, the following three species are mainly discerned:—(1) the common *Ricinus* plant, *Ricinus communis*, named by the Annamites Cây dú dú tía; (2) the green ricinus (*ricin vert*), *Ricinus viridis*, having the same local name; (3) the red ricinus (*ricin rouge*), *Ricinus sanguineus* (indigenous name, Cây dú dú dỏ).

The so-called "St. Eustatius" castor seeds appear to be obtained from *R. Zanzibarinus* or *R. Zanzibariensis.*[1]

The most important sources of castor seed are East India, Java,[2] the Mediterranean countries, Mexico, and the United States of America. By far the largest producer is East India. The exports of castor beans from India have grown considerably during the last fourteen years, whilst the Indian production of oil has decreased, owing to the expansion which the manufacture of castor oil has undergone in France, the United Kingdom, and the United States. This is illustrated by the following table:—

[1] Bloemendal, *Pharm.-Weekblad*, 42, 1905, 701.
[2] *Journ. Soc. Chem. Ind.*, 1895, 321.

Exports of Castor Beans and Oil from East India

Year ending March 31,	Castor Beans.	Castor Oil.
	Bushels of 50 lbs.	Gallons.
1890	2,003,973	3,198,787
1891	1,925,889	3,789,628
1892	1,872,472	3,929,758
1893	2,216,556	3,095,564
1894	2,481,369	2,754,261
1895	2,631,765	3,215,887
1896	2,348,201	2,420,358
1897	2,235,778	2,397,653
1898	2,372,516	2,344,797
1899	2,710,709	2,569,725
1900	1,978,731	1,833,842
1901	1,962,121	1,843,207
1902	2,965,527	2,424,270
1903	3,509,781	2,488,910
1904	3,509,717	2,300,015
1905	3,225,100	...
1906	2,867,500	...

The chief North American States in which castor seed is harvested are Oklahoma, (Eastern) Kansas, and (Western) Missouri. The bulk of the castor oil made in the United States is, however, derived from imported beans. The quantity of beans imported into the United States from India alone is shown in the following table, together with the amount of castor oil imported from East India :—

Imports of Castor Beans and Oil into the United States from East India

Year ending June 30,	Castor Beans.	Castor Oil.
	Bushels of 50 lbs.	Gallons.
1890	94,226	6,901
1891	105,374	2,073
1892	163,089	382
1893	147,061	286
1894	47,448	1,702
1895	277,231	28,846
1896	145,735	22,888
1897	84,128	4,368
1898	19,651	3,626
1899	25,003	7,615
1900	135,591	3,334
1901	191,288	3,206
1902	312,323	3,705
1903	380,270	6,643
1904	498,039	11,283

Considerable quantities of castor seeds are also exported from Mexico and Brazil. The exports from the latter country amounted to 2646 tons in 1905, and to 3126 tons in 1906.

The seeds consist of 20 per cent of husks, which are rich in mineral matter but contain no oil, and 80 per cent of kernels, forming a white softish mass. The whole seeds contain a toxic principle—the alkaloid "ricine."[1] They also contain a powerful fat-hydrolysing enzyme (see Vol. I. Chap. II.), which is made use of on a manufacturing scale for hydrolysing oils and fats for soap-making purposes (see Vol. III. Chap. XV.). The seeds contain 46 to 53 per cent of oil. Castor oil is produced on a large scale either by expression or by extraction. For the best quality of oil—for medicinal purposes—the seeds are first decorticated (shelled) by being passed between rollers set at such a distance that the outer shell only is broken. The kernels are then separated from the light husks by a blast of air in a specially constructed separator. Medicinal oil can only be prepared by expression in the cold, as the "ricine" does not pass into the oil under these conditions.

The once expressed cake is then subjected to a second expression, followed by a third expression. The oils so obtained are unfit for medicinal use, and are employed for manufacturing purposes. The cakes ("*castor pomace*," "*castor poonac*" in India) retain the poisonous alkaloid, and are therefore unfit for feeding cattle. Although attempts have been made to free the cakes from the ricine by washing with 6 to 7 times their amount of a 10 per cent sodium chloride solution (*O. Nagel*[2]), no castor cake is actually being used for feeding purposes.[3] The expressed cakes (just like the extracted meal; see below) are exclusively employed for manuring the land. The richness of castor cake in fertilising constituents has chiefly contributed to the growth of the castor oil industry in Marseilles, as the residual cakes are readily bought by the growers of early vegetables ("primeurs").

In India "poonac" is used principally for manure, but is also employed as fuel and for caulking timber, for the destruction of white ants and other pests, and for stuffing the soles of natives' shoes.

Marseilles has become one of the chief centres outside India for the production of castor oil. The importance of the castor oil and cake industry in Marseilles may be gathered from the following table:—

Imports of Castor Seeds into Marseilles

Year.	Double (metric) cwts.
1896	283,960
1897	149,270
1898	258,880
1899	259,830
1900	159,420
1901	259,310

[1] Cp. Osborne, Mendel, and Harris, *Zeit. f. analyt. Chem.*, 1907 (46), 213.

[2] *Journ. Soc. Chem. Ind.*, 1902, 30.

[3] With regard to the poisonous properties of castor seed, cp. Kobert, *Pharm. Zeit.*, 1906, 1062. Cp. also F. Schmidt, *Zeit. f. öffent. Chem.*, 1908, 245.

Imports of Castor Seeds into Marseilles—continued

Year.	Double (metric) cwts.
1902	262,140
1903	215,570
1904	144,070
1905	138,050
1906	135,540
1907	163,700

Since the finally pressed cake still contains about 8 per cent of oil, it is usually ground to meal, and extracted with carbon bisulphide in order to recover this amount.

On a large scale, about 40 per cent of oil is obtained by expression, 33 per cent being yielded by the first expression, and the remainder by the following expressions. Whereas formerly most of the castor oil was obtained by expression—in fact, the whole of the castor oil exported from India is expressed oil—the process of extraction has gained ground, notably in Hull (England) and in Boston (United States). The expansion of the extraction process is, to a large extent, due to the deterioration of the Indian seed, which has occurred during the last ten years (owing to the variation of the crops, and also to insufficient attention to the cultivation [1]). Hence inferior qualities are no longer used for the preparation of medicinal oil by expression in the cold, but are straightway treated with solvents for the complete extraction of the oil. The extracted oil can, of course, only be used for manufacturing purposes.

The process of refining castor oil consists chiefly in the removal of albumen by steaming the oil. The albumen, and especially those portions of the enzyme which have passed into the oil, are thereby coagulated, and then removed by filtering. Properly refined castor oil keeps very well,[2] and does not easily turn rancid, as observations in the author's laboratory have shown. A sample exposed to the atmosphere for four years contained only 1 per cent of free fatty acids.

Most commercial samples contain, therefore, only very small proportions of free fatty acids, as is evidenced by the numbers collated in the following table :—

[1] Java seed, which is properly attended to by the growers, yields therefore at present a better oil.

[2] Additional proof for this may be found in the statement made by Berthelot that the oil employed by the Egyptians for embalming was castor oil.

Free Fatty Acids in Castor Oil

Description of Oil.	No. of Samples.	Free Fatty Acids, calculated to Oleic Acid.	Observer.
		Per cent.	
Expressed oil . .	9	0·68-14·61	Nördlinger
Extracted oil . .	5	1·18-5·25	,,
Commercial oil .	2	1·46-2·16	Thomson and Ballantyne
Indian oil . .	23	0·14-1·06	Deering and Redwood

Castor oil is a colourless or pale greenish oil, having a taste at first mild, then harsh; this harsh taste is more pronounced in American than in Italian or French oils. The oil is very viscous. Contrary to older statements, it does not dry even when exposed in thin layers. A sample of medicinal oil, which the author kept exposed for four years, had its specific gravity increased from 0·9591 to 0·9629 (the iodine value had *not*, however, decreased).

An inquiry into the changes which castor oil undergoes on blowing with air, is being carried out in the author's laboratory. The results obtained so far (unpublished experiments) are detailed in the following tables:—

Blown Castor Oil (Lewkowitsch)

	Original Oil.	Blown 2 Hours at 150° C.	Blown 4 Hours at 150° C.	Blown 6 Hours at 150° C.	Blown 10 Hours at 150° C.
Colour	very light	light	light	light	orange yellow
Specific gravity at 60° F. . .	0·9623	0·9663	0·9798	0·9778	0·9906
Acid value.	1·1	1·3	2·4	2·6	5·7
Saponification value . . .	179·0	182·3	185·2	184·8	190·6
Iodine value	...	83·5	79·63	78·13	70·01
Acetyl value	146·9	150·7	154·3	159·0	164·8
Saponification value of acetylated oil	303·9 304·3	306·5 306·0	308·3 308·7	308·3	311·0

[TABLE

Blown Castor Oil Fatty Acids (Lewkowitsch)

	Original Fatty Acids.	Blown 2 Hours at 150° C.	Blown 4 Hours at 150° C.	Blown 6 Hours at 150° C.	Blown 10 Hours at 150° C.
Colour	clear	yellow	dark	very dark	black
Specific gravity at 60° F.	0·9543	0·9507	0·9529	0·9525	0·9561
Acid value	174·7	149·3	128·5	112·2	93·73
Neutralisation value	176·5	173·7	177·5	177·3	181·1
Iodine value	...	86·51	86·77	85·14	85·23
Acetyl value, after removal of some solid fatty acids[1] (dihydroxystearic)	133·1	94·26	105·5	93·31	81·4
Saponification value of acetylated acids	299·2	284·4	272·6	272·3	264·9

The figures obtained by *Procter* and *Holmes*[2] on blowing (English pressed) castor oil are subjoined :—

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0[3]	0·958	1·4800	83·0
3	0·958	1·4800	83·0
6	0·958	1·4802	74·0
9	0·958	1·4804	73·0
12	0·961	1·4804	72·0
15	0·962	1·4805	71·0
18	0·965	1·4805	71·0
21	0·966	1·4806	69·0
24	0·967	1·4807	68·0

As *Peter* has shown first, castor oil is strongly dextro-rotatory. This is confirmed by *Deering* and *Redwood*, who observed a strongly marked rotatory power in the twenty-three samples of Indian castor oil they examined. The rotation caused by 200 mm. of oil varied from + 7·6° to + 9·7° in a *Hoffmann-Laurent* polarimeter. The optical activity is no doubt due to the presence of an asymmetric carbon atom in ricinoleic acid (cp. Vol. I. Chap. III.).

If castor oil is allowed to stand in the cold, 3 to 4 per cent of a solid mass is deposited, consisting, according to *Krafft*,[4] of tristearin and triricinolein, palmitin being absent. Amongst the solid fatty acids *Juillard* discovered dihydroxystearic acid (the first natural hydroxy fatty acid) to the extent of 1 per cent. The chief constituent of castor oil is triricinolein. Triricinolein is, according to *Krafft*, solid in

[1] The acetyl value of the removed solid fatty acids was 143·3 (theory for dihydroxystearic acid : 280·5). From these acids there was obtained an acid of the melting point 130° C. (melting point of dihydroxystearic acid 131° C.), insoluble in petroleum ether.

[2] *Journ. Soc. Chem. Ind.* 1905, 1287.

[3] Original castor oil.

[4] *Berichte*, 1888, 2730.

its pure state; and accordingly the liquid state of castor oil would have to be ascribed to a state of superfusion of the oil. *Hazura* and *Grüssner*, however, have shown that the liquid fatty acids from castor oil consist of two isomerides, ricinoleic and isoricinoleic acids; *Krafft's* solid acid is, perhaps, identical with one of these acids (cp. also Chap. III. *Mangold*). Olein does not occur in castor oil.[1] Castor oil may therefore be said to consist of a small quantity of tristearin, of the glyceride of dihydroxystearic acid, and the glyceride of ricinoleic acid, all the isomerides being comprised under that term.

The presence of stearic acid, ricinoleic acid, and hydroxystearic acid in castor oil has been confirmed by *A. Haller*.[2] So far, however, he has been unable to confirm *Hazura* and *Grüssner's* statement that two isomeric ricinoleic acids occur in castor oil (cp. Vol. I. Chap. III.).

The proportion of triricinolein calculated by the author from the acetyl value of castor oil, 150, would be $\frac{(3\times 298+38)\times 15}{168\cdot 3} = 83\cdot 1$ per cent. Since dihydroxystearic acid—present to an extent of 1 per cent amongst the fatty acids—has the acetyl value 281·9, the percentage of ricinolein can only be about 82. The iodine value of triricinolein being 81·76, the above calculated 82 per cent of triricinolein would absorb 67 per cent of iodine. Castor oil must therefore contain some less saturated fatty acids than ricinoleic. This is indeed borne out by the iodine value of the liquid fatty acids having been found to be 106·9.

On reducing castor oil with hydrogen in the presence of colloidal palladium in the cold, *Paal* and *Roth*[3] obtained a solid fat softening at 69° C. and melting at 77° C. The iodine value of the reduced glyceride was 1·9, and would thus appear to consist of saturated glycerides. The castor oil had thereby become difficultly soluble even in hot alcohol; the number of c.c. of hydrogen absorbed being 32·86 c.c. for half a gram, theory requiring 36·8 (cp. Vol. I. Chap. I.).

The amount of unsaponifiable matter in the samples examined by *Thomson* and *Ballantyne* varied from 0·30 to 0·37 per cent.

The specific gravity of castor oil, its behaviour with solvents, its acetyl value, and its very high viscosity afford ready means of identification.

Castor oil has the highest *specific gravity* of any natural fatty oil; only the "blown oils" (Chap. XV.) acquire so high a gravity in the course of manufacture. Hence the presence of a foreign fatty oil in castor oil would, in the first instance, be recognised by a lower gravity of the sample than 0·960. Rosin oil of specific gravity 0·998, which may have been added to an adulterated oil in order to mask the influence of a foreign fatty oil, can be easily detected by determining the unsaponifiable matter quantitatively.

[1] Hazura and Grüssner, *Journ. Soc. Chem. Ind.* 1888, 681.
[2] *Comptes rendus*, 144 (1907), 462. [3] *Berichte*, 1908, 2283.

Physical and Chemical Characteristics of Castor Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15·5	0·960-0·966	Allen	-- 10 to – 12[2]	Schaedler	181	Dieterich	84·4	Hübl	1·1	Lewko-witsch
,,	0·9591[6]	Lewkowitsch			180-183	Itallie	84-84·5	Dieterich		
,,	0·9653-0·9679	Thomson and Ballantyne			178·6-180·2	Thomson and Ballantyne	83·6-83·9	Thomson and Ballantyne		
,,	0·9637-0·9642	Deering and Redwood[1]			176·7-179·1	Deering and Redwood[1]	83·8-85·9	Itallie		
18	0·9602	Long			185·9-186·6	Henriques[3]	83·7-85·3[4]	Deering and Redwood[1]		
20	0·9589	,,			183·3[5]	Lewkowitsch	81·4[5]-90·6[6]	Lewkowitsch		
,,	0·963-0·965	Itallie					86·2-87·1	Wijs		
23	0·964	Dieterich								
25	0·9555	Long								
30	0·9522	,,								
35	0·9488	,,								
94	0·9081	Saussure								
99	0·9096	Allen								
(water at 15·5 = 1)										

[1] Twenty-three samples of Indian oil, *Journ. Soc. Chem. Ind.* 1894, 959. [2] American oil, which is richer in solid glycerides than Indian or Italian oils.
[3] Java oil. [4] Calculated from bromine values, 52·8-53·7. [5] Calcutta oil, second pressing. [6] Medicinal oil.

Physical and Chemical Characteristics of Castor Oil—continued

Acetyl Value.		Thermal Tests.				Refractive Index.			Viscosity in Redwood's Viscosimeter.	
		Maumené Test.		Heat of Bromination.						
	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 100° F.	Observer.
149·9	Lewkowitsch	47	Maumené	15	Hehner and Mitchell	15	1·4795-1·4803	Strohmer	1160-1190	Deering and Redwood
150·5	,,	46	Archbutt	14·7	Jenkins	20	1·4783-1·4789	Harvey		
						60	1·4636	Thoerner		

Oleo-refractometer.	
"Degrees" at 22° C.	Observer.
+43 to +46[1]	Jean
+ 37	Bruyn and van Leent
+ 40	,, ,,
+41 to +42·5	Deering and Redwood
+39 to +42	Pearmain

Specific Temperature Reaction.	
89-92	Thomson and Ballantyne

Butyro-refractometer		
At °C.	"Degrees."	Observer.
25	78	White
40	65·5	,,

[1] Java oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
15·5	0·9509	Allen	3	Hübl	13	Hübl	290-295	Alder Wright	86·6-88·3	Morawski and Demski	1·4546	Thoerner
98-99	0·8960	,,					306·6	Allen	87-88	Thoerner		
							292	Williams				
									Liquid Fatty Acids.			
									106·9[1]	Tortelli and Ruggeri		

[1] Italian oil, 1898 crop; iodine value of oil, 87·4.

Castor oil has the highest *viscosity* of all known oils, only "blown oils" (Chap. XV.) and rosin oil approaching it in this respect. The viscosity of the twenty-three samples examined by *Deering* and *Redwood* was from 1160 to 1190 seconds for 50 c.c. at 100° F.

Castor oil is miscible in every proportion with glacial acetic acid and **absolute alcohol.** It also dissolves, at 15° C., in 2 volumes of 90 per cent, and in 4 volumes of 84 per cent alcohol. *Van Itallie*[1] has determined the solubility, in 90 per cent alcohol, of five samples of castor oil (three of which, A, B, C, had been expressed in the laboratory at the temperatures of 20° C., 50° C., and 80° C. respectively, whereas D and E were commercial oils), with the following result :—

10 c.c. of Oil.	Require 90 per cent Alcohol at 20° C. c.c.
A	26·4
B	26·8
C	27·8
D	29·4
E	24·0

For the rapid examination of castor oil (as by custom-house officers), *Finkener*[2] recommends agitation of 10 c.c. of the sample with 50 c.c. of alcohol of the specific gravity 0·829 at 17·5° C., in a graduated cylinder. A strong turbidity, which does not disappear even at 20° C., shows that the oil is not pure ; even 10 per cent of foreign oils (as sesamé, linseed, rape, cotton seed oils) may thus be detected.

Castor oil is nearly insoluble in large quantities of **petroleum ether,** kerosene, and higher boiling paraffin oils. At a temperature of 16° C. as little as 0·5 per cent of castor oil in these solvents causes a turbidity. However, castor oil gives a homogeneous solution with an *equal* measure of petroleum ether, or a volume and a half of kerosene or paraffin oil ; if more of the solvents is used, any excess will float on the top of the mixture. The characteristic insolubility is lost at the ordinary temperature if castor oil be adulterated with a small quantity of a soluble oil.

Castor oil is distinguished from all other oils—with the exception only of grape seed oil (pending further examination of grape seed oil) —by its high *acetyl value.* In the case of castor oil the acetyl value is an important "characteristic." Its determination furnishes, therefore, the surest means of ascertaining purity, and enables the analyst to estimate the amount of adulteration.

The saponification value also (approaching that of the oils belonging to the rape oil group) and the *iodine value* will afford means of detecting fraudulently added oils.[3]

In the *elaïdin test* castor oil gives a whitish solid mass, due to the formation of ricinelaïdin.

[1] *Chem. Zeit.* 1890, Rep. 367. [2] *Journ. Soc. Chem. Ind.* 1887, 148.

[3] The saponification and iodine values given by Thoerner, viz. 201-203 and 93-94 respectively, are so abnormal that I have omitted them from the table of characteristics.

The price of castor oil is at present so low that adulteration with a fatty oil will hardly be practised. Still, at times when castor oil was much higher in price, adulteration with rape oil, rosin oil, and chiefly with blown oils, did occur.

Rosin oil would be easily detected by determining the unsaponifiable matter. Obviously, the polarimetric examination of the sample, if rosin oil be present, will be useless.

The "**blown oils**," although simulating castor oil in specific gravity and viscosity, differ from it in having much lower acetyl values, higher saponification values (see Chap. XV.), and lesser solubilities in alcohol.

Castor oil is easily detected in other oils by the high acetyl value and the high specific gravity of the sample.

On nitrating castor oil with concentrated nitric and sulphuric acids, "nitrated" castor oil is obtained (cp. Chap. XV.).

Castor oil is used in medicine (the purgative action of the oil being due to ricinoleic acid). Recently attempts have been made to convert castor oil into medicinal preparations, having the form of powders (see Vol. III. Chap. XV.).

Next in importance is the employment of castor oil for the manufacture of Turkey-red oils ("alizarine assistant") and of "Emulsified Oils" (Vol. III. Chap. XV.). On saponification with soda, castor oil yields a hard soap which requires very large quantities of salt (like cocoa nut oil) for "salting" out. It is, therefore, little used alone in the manufacture of hard soaps. The soda soap has, however, the property of imparting transparency to soaps; hence castor oil is largely employed in the manufacture of transparent soaps.

In India the oil is largely employed as a lubricant for locomotive bearings, but in this country it is too thick to be serviceable for this purpose. It is, however, used for lubricating marine engines.

Castor oil is used largely as a preservative for leather belting in heavy work, and for fat liquoring in the leather industries. It also plays an important part in the preparation of fly-gums and in the manufacture of other adhesive agents.[1] Recently castor oil has been proposed as a substitute for camphor in the manufacture of celluloid.[2]

On a smaller scale castor oil is subjected to destructive distillation for the preparation of "cognac oil," when undecylenic acid and œnanthaldehyde pass over, whilst the remaining mass solidifies to a very bulky, spongy, indiarubber-like mass, for which a solvent has not yet been found.[3]

The residue, after successive washings with alcohol, chloroform, and ether, was found to have the composition [4] $C_{33}H_{58}O_5$, corresponding to the anhydride of triundecenoic (triundecylenic) acid, $(C_{11}H_{20}O_2)_3 - H_2O$. On melting the product with potassium hydroxide, it yields hexa-

[1] Cp. Castle, English patent 6936, 1905; Patat and Co., French patent 361,954 (gum tragasol and castor oil).

[2] C. Gillet, French patent 382,270.

[3] *Berichte*, 1876, 2034.

[4] Fendler and Thoms, *Archiv d. Pharm.* 1901 (239), 1.

decenoic acid (hexa-undecylenic acid), $C_{16}H_{30}O_2$. On oxidising with fuming nitric acid, sebacic acid and an acid of the formula $C_{13}H_{22}O_4$ were obtained; by oxidation with potassium permanganate, sebacic acid and lower fatty acids were produced. If the distillation of castor oil be stopped just before the mass would have become converted into the indiarubber-like substance, the oily residue still contains glycerides. This residue corresponds to the composition $C_{105}H_{148}O_{18}$, which appears to be the glyceride of the dibasic triundecenoic (triundecylenic) acid $—(C_3H_5)_2(C_{33}H_{58}O_6)_3$ (cp. Chap. XV. "Polymerised Oils").

Castor oil becomes also polymerised by heating for 10 hours to 260°-300° under a pressure of 4-6 atmospheres; it thereby becomes miscible with mineral oils.[1]

Lesser known non-drying oils, see table opposite.

2. ANIMAL OILS

In this section the oils obtained from animals are described under the following two classes :—

(1) Marine animal oils,
(2) Terrestrial animal oils.

This subdivision is not made merely for the sake of convenience; it is based on striking chemical differences. Broadly speaking, these two groups may be compared with the two large classes of vegetable oils—the drying and the non-drying oils.

Like the drying oils the marine animal oils are characterised by very high iodine values, by the large amount of ether-insoluble bromides they yield, by their power of absorbing oxygen, and by not yielding elaïdins.

The majority of the terrestrial animal oils resemble the non-drying oils in that they have low iodine values, do not easily absorb oxygen, and yield solid elaïdins.

Just as amongst the vegetable oils there are a number of them occupying an intermediate position between the drying and the non-drying oils, viz. the semi-drying oils, we find among the marine animal oils gradations from the most pronounced type of easily oxidisable oils to those containing large quantities of glycerides of saturated fatty acids, thus approaching the chemical constitution of terrestrial animal oils.

Similarly, such intermediate oils may be expected amongst the oils from terrestrial animals. Hitherto, only one oil—chrysalis oil —has been described somewhat fully. It may be looked upon as a representative of semi-drying animal oils (cp. also "Drying Animal Fats" and "Semi-Drying Animal Fats."

[1] English patent 24,935, 24,936, 1905.

	Yield Per cent.	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids. °C.	Observer.
	0·87	227	82	10	Heinisch and Zellner [1]
	...	...	87·0	12·5	Milliau [2]
	...	211·0	83·6	...	Lidoff [3]
	...	198·57	83·1	...	Niederstadt [4]
	...	170·1 (?)	65·1	...	O. May [6]
	27·11 [7]	224·72	62·3	...	Niederstadt
	...	179·84	60·6	...	,,
	5·5	...	...	...	Lecomte and Hébert [8]
go	20	...	...	...	Power and Lees
	22·2	185·4	81·5	...	Power and Salway [10]
	45·6	284·4	...	...	Caspari [11]
	9·1	200	86-87·9	...	Frankforter and Martin [13]

about 90 per cent of oleic acid and 10 per cent of palmitic acid. Further data given
refractive index at 20° C., 1·460-1·470. With regard to the oils obtained from other
avaria flava, *Lycoperdum gemmatum*, cp. Zellner, *Monatsh. f. Chemie*, 1906 (27), 295.
ohol, at 74° C.
richte d. deutsch. pharm. Gesell. 1902, 144.
to consist of oleic acid, stearic acid, and palmitic acids.
nall quantities of myristin are admixed. The oil occurs in the rhizome of the plant.
ises, Paris, 1902, p. 1.
e Dutch East Indies the fruits are known as *bidji makasar* and *tambara maridja*. They

ic, stearic, oleic, and small quantities of linolic acids. The oil yields further small
lting at 135-136° C., was isolated.
f capric, lauric, and oleic acids, laurin preponderating.
is 1·48821, and at 15° C., 1·48228. The husks yielded to ether 8·5 per cent of a

[13] *Amer. Journ. Pharm.* 76, 151.

(1) Marine Animal Oils

The members of this class may be conveniently subdivided into the following three groups :—

α. Fish oils.
β. Liver oils.
γ. Blubber oils.

The term "train oil" has been avoided, as its German equivalent "Tran" includes all three groups, and is therefore apt to cause confusion. It must further be premised that, under blubber oils, those oils only are included which consist wholly or in greater part of glycerides. Therefore the liquid waxes—viz. sperm oil and Arctic sperm oil, which are frequently classed together with blubber oils—are excluded from this group, since, according to their chemical constitution, they must be placed amongst the waxes proper.

The oils belonging to this class are liquid at the ordinary temperature, yielding, however, on cooling, varying amounts of solid glycerides. They are readily distinguishable from other liquid fats by their fishy taste and smell.

The specific gravities of the marine animal oils vary between 0·916 and 0·930. The saponification values of some of the blubber oils deviate widely in both directions from the mean value of the vegetable oils—195—according as they contain large amounts of spermaceti or of glycerides of volatile fatty acids. Hence this characteristic cannot be used as a basis for subdivision.

The liver oils, however, appear to form a natural group characterised by notable amounts of cholesterol and other foreign substances. Since, for the purposes of subdivision, I adopt the iodine value as the basis, the liver oils may be interposed between the fish oils and the blubber oils.

The earlier statements that the marine animal oils are characterised, and can be differentiated from all other fatty oils, by the intense colourations they give with caustic soda, sulphuric acid, nitric acid, and phosphoric acid, must be considered as valueless.

Phosphoric acid, in particular, was proposed as a very characteristic reagent, capable of detecting even 0·1 per cent of these oils in vegetable oils. The best results were stated to be obtained by warming five measures of the oil under examination with one volume of syrupy phosphoric acid, when all oils belonging to this class, both in their pure state or in admixture with other oils, were said to show intensely red, reddish-brown, or brownish-black colourations. *Holde*[1] stated that the phosphoric acid test was uncertain, as on the one hand rosin oils produce red colourations with this acid, and on the other hand distinct colourations only appear when large quantities of

[1] *Journ. Soc. Chem. Ind.* 1890, 419.

marine animal oils are present in other oils. The author,[1] after an exhaustive examination of these colour reactions, has come to the conclusion that they are by no means characteristic of these oils, but are due to impurities which can be removed by proper modes of refining. Thus, a sample of horses' foot oil (not refined), prepared in my laboratory, gave, with the above-mentioned reagents, colourations which might be considered as typical of marine animal oils. Also *old* samples of linseed and cotton seed oils behaved similarly.

The same conclusion holds good of the chlorine test.

Owing to the large amount of unsaturated fatty acids which the oils belonging to this class contain, they develop a considerable amount of heat in the thermal tests. They also absorb notable amounts of oxygen without, however, drying to a flexible skin like the best drying vegetable oils do.

The nature of the fatty acids in these oils is very imperfectly known. Some of them have high *Reichert* values, pointing to the presence of large quantities of volatile acids. On cooling, others deposit "stearine," which appears to consist chiefly of palmitin. Most of these oils consist of glycerides of unsaturated fatty acids, as is shown by their high iodine values, ranging from 120 upwards. These high iodine values, especially those of the fish and liver oils, clearly point to the presence of acids less saturated than those belonging to the oleic series. It is by no means certain that oleic acid occurs in these oils. The physetoleic acid of the earlier authors could not be detected by *Fahrion*.[2] *Bull's*[3] statement that all oils belonging to this class—with the exception of cod liver oil—contain erucic acid, as also an acid of the formula $C_{20}H_{38}O_2$, requires confirmation; all the more so, as *Bull*[4] has shown more recently that erucic acid does occur in cod liver oil (see below), and as the various highly unsaturated acids mentioned by him could not be found by *Tsujimoto* (see below). The less saturated acids in these oils cannot be identical with linolic or linolenic acids, as the oils, although absorbing large amounts of oxygen, do not dry like linseed oil.[5] In the bromide test the marine animal oils yield considerable amounts of brominated glycerides. These differ, however, from the ether-insoluble bromides obtained from vegetable drying oils; for the ether-insoluble bromides prepared from the mixed fatty acids (in the same manner as linolenic [ether-insoluble] bromide is obtained) do not melt, like linolenic [ether-insoluble] bromide, at about 175° C., but remain solid up to even 200° C., when the mass becomes black, without, however, melting to a liquid (cp. Vol. I. Chap. VIII.).

Fahrion[6] is of opinion that he has proved the presence of an unsaturated acid, $C_{18}H_{30}O_2$—jecoric acid—(cp. Chap. III.), and infers the presence of an unsaturated acid of the composition $C_{17}H_{32}O_2$—

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1894, 617. Cp. vol. i. chap. vii.

[2] *Journ. Soc. Chem. Ind.* 1893, 938; 935. [3] *Chem. Ztg.* 1899, 996.

[4] *Berichte*, 1906, 3570.

[5] The free fatty acids from seal and cod liver oils kept in stoppered glass bottles deposit, after a few months' standing, a resinous substance (Lewkowitsch).

[6] *Journ. Soc. Chem. Ind.* 1893, 938; 935.

asellic acid—from a dihydroxylated acid (dihydroxyasellic acid) obtained on oxidising the fatty acids of sardine oil. In the light of *Ljubarsky's* statement (Vol. I. Chap. III. "Dihydroxypalmitic Acid") that dihydroxystearic acid forms with dihydroxypalmitic acid a compound behaving like a chemical individual (termed by me a "eutectic" compound), the existence of dihydroxyasellic and hence of asellic acid itself must be doubted. *Heyerdahl* claims to have discovered two unsaturated acids in cod liver oil, viz. jecoleic and therapic acids (Vol. I. Chap. III.). *Bull* assumes amongst the liquid fatty acids of cod liver oil the presence of an acid of the composition $C_{23}H_{36}O_2$, belonging to the series $C_nH_{2n-10}O_2$. The existence of all the last-mentioned acids is so far hypothetical. An investigation of this subject was therefore a desideratum.

Since then *Tsujimoto*[1] has shown that the fish and blubber oils contain clupanodonic acid of the formula $C_{18}H_{28}O_2$, an acid which yields in the bromide test an octobromide (cp. Vol. I. Chap. VIII.), and *Bull*[2] has stated that a new acid, gadoleic acid, $C_{20}H_{38}O_2$, occurs in notable quantities in herring oil, cod liver oil, and whale oil. Moreover, *Tsujimoto* has thrown considerable doubt on the occurrence of jecoric acid in herring oil, and has further shown that no evidence could be obtained of the presence of the two highly unsaturated acids of the formulæ $C_{22}H_{32}O_2$ and $C_{24}H_{40}O_2$, stated by *Bull* to occur in herring oil. The existence of the octobromide of clupanodonic acid explains satisfactorily the different behaviour of the insoluble bromides, yielded by these oils, from the linolenic bromide (see above).

Halphen[3] recommends as a general test for the presence of marine animal oils, a reagent consisting of 28 volumes of glacial acetic acid, 4 volumes of nitrobenzene, and 1 volume of bromine. This reagent differs from the one employed in the bromide test merely by the presence of nitrobenzene. Evidently Halphen's method does not admit of a differentiation of marine animal oils from vegetable drying oils. The same stricture holds good for the further suggestion made by *Halphen*, to differentiate the ether-insoluble bromides obtained from linseed oil on the one hand, from those yielded by marine animal oils on the other, by their behaviour with boiling carbon tetrachloride. Experiments made in the author's laboratory have proved that the ether-insoluble bromide from linseed oil does dissolve in hot carbon tetrachloride, and gives a somewhat crystalline precipitate on cooling, whereas the ether-insoluble bromide from marine animal oils does not dissolve completely and gives a gelatinous precipitate on cooling. It would, however, be impossible to differentiate thus linseed oil from marine animal oils; it is still more hopeless to detect thus marine animal oils in linseed oil. The differences in the melting points of the ether-insoluble bromides of the mixed fatty acids are so characteristic that we can dispense with the *Halphen* solubility test.

[1] *Journal of the College of Engineering*, Tokyo Imperial University, vol. i. 1906.
[2] *Berichte*, 1906, 3574.
[3] *Journ. Pharm. Chim.* 1894, 359; 391.

α. Fish Oils

The fish oils are obtained from all parts of the body of common fish—such as the herring, sardine, salmon, sprat, etc.—by boiling. The livers of these fish contain, as a rule, very little oil, whereas the bodies of the liver-oil-yielding fish, notably cod fish, yield so little oil, that it is not prepared commercially. Cod fish only contains 1·8 per cent, and ling fish 2·2 per cent of oil.[1]

It should be noted that the industry of fish oils has undergone a very important change during the last decade, in consequence of the replacement of fishermen's sailing boats by steam trawlers. Whereas in former times fishing boats would remain out at sea for about a week or two, the fish are at present brought to shore (*i.e.* into the rendering establishment) almost within one day. Thus deterioration due to the oil having remained for some time in contact with highly putrescible matter, has been obviated to a large extent. The very dark colour and rank odour which used to characterise fish oils has therefore given place to a somewhat paler colour and a much less unpleasant, though still strongly pronounced, fishy smell. Oils so obtained lend themselves readily to refining operations; it may, however, be mentioned that special processes applied by the author on a large scale to oils of rank odour have brought even these oils within the reach of industrial application.

It should further be noted that in consequence of these improvements, as also in consequence of the erection of establishments in which rendering is conducted on such a large scale that the separation of livers from the bodies of oil-yielding fish is performed more carefully, commercial fish oils are now comparatively free from liver oils, which were so prevalent in the fish oils of former years. The analytical numbers published by earlier observers frequently referred to a mixture of fish and liver oils, a fact which found its readiest expression in the large amount of unsaponifiable matter stated to have occurred in fish oils. These unsaponifiable matters were due to the presence of liver oils, as also of liquid and solid waxes, which were intermixed with the fish oils. Hence those numbers which appeared to the author unreliable have been omitted from the following pages.

Frequently attempts have been made to deprive the fish oils of their peculiar fishy taste, so as to bring them within the range of edible oils.[2] All these endeavours have failed hitherto, but the tempting nature of the problem is still attracting the attention of inventors. *A. de Hemptinne* has recently patented a process[3] of treating fish oils with ozone, with a view to removing their peculiar taste. I can state from my own experience with samples treated by this process, that it does not appear unpromising, but hitherto oils so treated have not appeared on the market.

[1] Greshoff, *Chem. Zeit.* 1906, 856.

[2] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.* 1903, 592.

[3] English patent 12,525, 1905; German patent 169,410.

Less deserving of attention are the processes aiming at the treatment of fish oils or their fatty acids with concentrated sulphuric acid,[1] or with sulphuric acid and sodium nitrate.[2] *E. Böhm*[3] claims to deodorise fish oils by heating them *in vacuo* to a temperature of 350° to 400° C. *E. Petersen* and *H. Holstein*[4] treat with superheated steam and char and chalk. *Bottaro*[5] states that odourless fish oil fatty acids are obtained by saponification with lime and by decomposing the lime soap with sulphurous acid.

The chief centres of the fish oil industry are the northern ports of the east and west coasts of Great Britain, Gloucester on the east coast, and San Francisco on the west coast of the United States, and the east and west coasts of Canada. Japan is at present making great efforts to place its fish oil industry on a proper commercial basis. Smaller quantities of oils are furnished by the sardine packing works, in which sardine oil is prepared as a by-product, and by some minor installations, such as an establishment in Alt-Pillau (East Prussia), where miscellaneous fish caught in the Baltic are worked up by maceration between rollers, drying of the comminuted mass, and extraction with "benzine."

If fish oils are allowed to stand for some time, especially at low temperatures, larger or smaller quantities of "stearine" separate. This "stearine" ("fish stearine") is collected separately (cp. Vol. III. Chap. XVI.).

MENHADEN OIL

French—*Huile de menhaden; Huile d'Alose.* German—*Menhadenöl.* Italian—*Olio di menhaden.*

For table of characteristics see p. 340.

Menhaden oil is an American fish oil, and, like other fish oils, is prepared from the body of fish, especially from that of the menhaden, *Alosa menhaden*, Cuv. (*Brevoortia tyrannus*), a fish somewhat larger than a herring. From about May until November this fish appears in enormous quantities off the Atlantic coast (especially of New Jersey), so that as much as 400,000 tons are caught in one season.

The fish are delivered from the steamers, by means of elevators, on to automatic conveyors, from which they are passed over automatic scales into large boiling pans. These are provided with false bottoms, below which open steam-coils are fixed. On boiling the contents of the pan, the fish are disintegrated and the oil separates easily from the flesh. After turning off the steam and allowing the mass to rest, the oil rises to the top and can be easily skimmed off by means of swivel skimmers.

During the last few years boiling vessels have been introduced which permit of continuous working, the fish being passed on con-

[1] Sandberg, German patent 162,638. [2] Potolowsky, United States patent 823,361.
[3] English patent 7901, 1906. [4] German patent 202,576, 1908.
[5] English patent 23,534, 1906.

veyors through the boilers continuously,[1] whilst open steam acts on the fish. The time required for the fish to pass lasts from fifteen to twenty minutes. The whole mass is then transported by screw conveyors into settling tanks, where the oil separates by gravitation. In either process the "fish scrap" falls to the bottom of the vessels, and is then pressed in hydraulic presses, similar to those used in the working up of "tankage" (see Vol. III. Chap. XVI.), when a further quantity of oil—inferior in colour—is obtained. In some works such pressed cake—termed "chum"—is boiled out with hot water and pressed once more; but this process, being unremunerative, is not carried out in large works. The scrap is finally dried in continuous dryers, of which various types are in use (*Anderson* dryer, *Cummer* dryer, vacuum dryers), and is sold as a valuable manure. In fact the "scrap" was formerly considered as the main product, and it is owing to the demand for scrap that the fish oil industry has assumed such large dimensions. As the fish contain only from 1 to 16 per cent of oil—rarely more—processes for its recovery from the scrap by means of solvents[2] (see this Vol. Chap. XIII.) are most unlikely to prove remunerative, considering the enormous quantities of fish that must be dealt with.

With the extension of the industry, new uses have been found for the oil itself, which now ranks equal in value to the scrap.

In order to show the extent of the menhaden fish oil industry, the following table, published by the United States Fish Commission of Washington, is given:—

State.	Year.	No. of Works.	Number of Fish worked up, in Thousands.	Oil Produced.		Fish Scrap Produced.		Value of Total Production.
				Gallons.	Value in Dollars.	Tons.	Dollars.	Dollars.
Rhode Island	1902	1	114,758	897,188	225,912	..	..	439,818
Connecticut	1900	2	19,976	118,750	30,475	450	12,000	65,925
New York	1902	3	187,671	1,397,583	353,279	9,030	218,217	664,261
New Jersey	1901	6	27,090	109,789	25,440	1,131	52,046	77,486
Delaware	1902	1	84,869	394,119	96,724	1,642	39,069	246,461
Virginia	1901	15	387,727	723,215	164,465	21,130	617,872	817,725
North Carolina	1902	7	70,168	102,052	22,730	1,884	40,214	127,072
Texas	1901	1	26,807	69,639	14,654	1,710	30,087	44,741
Total	..	36	910,066	3,812,335	933,679	36,977	909,505	2,473,489

The colour of menhaden oil varies in the first instance according to the state of freshness in which the fish arrives, and in the second

[1] Cp. English patent 25,425, 1901, F. V. Speltie, and German patent 151,553, F. V. Speltie; cp. also French patent 338,472, "Procédé et appareil pour la fabrication continue d'huile de poisson et de guano," H. J. A. Pompe van Meerdeervorte; German patent 135,566, Ch. Wacker; English patents 24,604, 1901; 18,743, 1902, E. R. Edson (in the name of Haddon); German patents 139,969; 141,595, 149,613, E. R. Edson; German patent 168,132, P. Hagen; English patent 25,882, 1906, Pearson.

[2] Cp. *e.g.* English patent 8483, 1901, "Delattre et la Société Anonyme d'Épuration des Eaux-Vannes," etc., and J. Carstairs; German patent 131,962, 1901.

instance with the duration of the boiling process. The longer the oil has been allowed to remain in contact with the putrescible mass and the longer the fish has been boiled, and hence the longer the oil has been in contact with the gluey water, the darker is its colour. Therefore, the separation of the oil from the gluey water is carried out as rapidly as possible. Fresh fish yield a light-coloured oil; the oil running from the "scrap" in the presses is the darkest in colour.

In commerce the following three qualities are known—"Prime Crude," "Brown Strained," and "Light Strained Oil." Frequently the oils are differentiated into four grades—*A*, *B*, *C*, and *D*; *A* being extra pale, *B* pale, *C* brown, and *D* dark brown oil. Since the menhaden oil industry has extended along the Atlantic coast even down to Texas, the trade differentiates also between Northern menhaden oil and Southern menhaden[1] oil. It is therefore desirable that in future the origin of an oil, the characteristic numbers of which are published, be described as fully as possible. The process of refining consists mainly in brightening the oil by filtering, etc.

The light-coloured oils are allowed to rest some time in the cold, whereby "stearine" separates; thus the "winter oils" are obtained. They are then bleached by filtering over fuller's earth, etc.; in this manner two grades are obtained, viz. "bleached winter white" and "bleached winter" oils.

Menhaden oil consists almost entirely of glycerides, as is shown by its saponification value, the proportion of glycerol it yields on saponification, and the small amount of "unsaponifiable matter." The chemical composition of the unsaturated glycerides is not known yet. *Bull* states that he isolated from a specimen of menhaden oil 23 per cent of a fatty acid, having the neutralisation value 197·0, and absorbing 312·5 per cent of iodine.

As clupanodonic acid absorbs theoretically 367·7 per cent of iodine, the acid isolated by *Bull* must have contained considerable quantities of clupanodonic acid.

The amount of unsaponifiable matter found by several observers is given in the following table:—

Unsaponifiable Matter

Colour of the Oil.	Per cent.	Observer.
Pale yellow	0·61	Fahrion
Red	0·82	,,
Yellowish-red (Levantine) .	1·43	,,
Brown	1·60	Thomson and Ballantyne
Extra pale	1·43	Bull

[1] Southern menhaden oil, "A" quality, is very pale, but contains more "stearine" than the Northern oil; as the trade term runs, it is more "tender" and congeals readily at low temperatures.

Physical and Chemical Characteristics of Menhaden Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Reichert Value.	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9311	Bull	−4	Jean	192	Allen	1·2	Allen
15·5	0·927-0·933	Allen						
,,	0·9311	Thomson and Ballantyne	...	...	189·3	Thomson and Ballantyne	...	...
					188·7	Bull		
					193 [1]	,,		

Physical and Chemical Characteristics of Menhaden Oil—continued

Iodine Value.		Maumené Test.		Butyro-refractometer.		
Per cent.	Observer.	°C.	Observer.	°C.	"Degrees."	Observer.
147·9	Archbutt	126	Allen	25	80·7	Liverseege [2]
160	Thomson and Ballantyne	123-128	Archbutt	40	71·3	,,
153·9	Schweitzer and Lungwitz	Specific Temp. Reaction.		40	72 [3]	Lewkowitsch
172·6	Bull					
139·2 [1]	,,	306	Thomson and Ballantyne			

[1] "Natural pressed" menhaden oil.

[2] *Analyst*, 1904, 211. The optical rotation of the sample examined was −1·0° in a 200-mm. tube, the Valenta test 80° C.

[3] Northern menhaden oil.

The unsaponifiable matter consists chiefly of cholesterol, to the presence of which the slight optical activity of menhaden oil is due. A sample examined by *Liverseege* showed in a 200-mm. tube a deviation of $-1°$; the same sample gave in the *Valenta* test 80° C.

Jean found in menhaden oil 0·02 per cent of iodine.

Menhaden oil is frequently adulterated with mineral and rosin oils.

Its principal use is in the currying trade, and in the manufacture of sod oil. The oil is also employed in soap-making, for the tempering of steel, and for adulterating Newfoundland cod liver oil and paint oils.[1]

JAPANESE SARDINE OIL, JAPANESE FISH OIL

French—*Huile de sardine du Japon.* German—*Japanisches Fischöl.* Italian—*Olio di sardine del Giappone.*

For tables of characteristics see p. 342.

Japanese sardine oil is obtained from *Clupanodon melanosticta*, T. and S. (Japanese: *ma-iwashi*), a fish belonging to the *Clupeidæ*. The fish is chopped and boiled with water, when the oil separates on the top. When there is a scarcity of labour—as happens during the fishing seasons—the fish is allowed to rot in heaps; the greater part of the oil then flows out and the remainder is subsequently recovered by pressure. The oil obtained by the first process is limpid and can be easily refined, whereas the oil from the second process has a very dark colour and a nauseous taste. The crude oil contains about 30 per cent of "stearine."[2] It is refined in Yesso and Yokohama by heating to 50°-60° C. for an hour, and then running it off into wooden vessels, where it separates into three layers. The upper layer is liquid and clear, the middle layer consists of solid fat,[2] and the lowest of water intermixed with albuminous substances and "scrap."

Owing to the extension of railway facilities the fish is now largely sold for food.

By far the greater part of sardine oil produced in Japan is exported to Europe. In 1905, 1430 tons (2,379,267 kin, valued at 125,260 yen) were shipped abroad. The remainder is used at home for tanning leather, preparing paints, etc.

[1] E. W. Mann, *Journ. Soc. Chem. Ind.* 1903, 1357, describes a menhaden oil containing 6·73 per cent of unsaponifiable matter, and having the Reichert value 2·2 and the iodine value 145·8. These abnormal numbers have not been embodied in the tables.

[2] This solid fat, brought into commerce under the name "refined fish tallow," is chiefly used as a *dégras* substitute for currying leather (*Journ. Soc. Chem. Ind.* 1894, 894). Cp. also Vol. III. Chap. XVI.

Physical and Chemical Characteristics of Japanese Sardine Oil

	Specific Gravity.			Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.		
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	20 °C.	1·4802-1·4808	Tsujimoto
Commercial Oil .	15	0·916	Fahrion	20-22	Villon	189·8-192·1	Lewkowitsch	121·5	Lewkowitsch	Butyro-refractometer.		
	,,	0·9272-0·9338	Bull	...	...	...	...	134·1-171·3	Bull	°C.	"Degrees."	Observer.
Oil from *Clupanodon melanosticta*	15·5	0·9316-0·9347	Tsujimoto	...	...	194·8-196·2	Tsujimoto	180·6-187·3	Tsujimoto	40 40	56 61	Lewkowitsch ,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Fatty Acids +Unsaponifiable.		Solidifying Point. Titer Test.		Melting Point. Capillary Tube.		Ether-insoluble Bromides.	
	Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Commercial Oil	94·5-95·3	Fahrion	28·2	Lewkowitsch	...	...	...	...
Oil from *Clupanodon melanosticta* .	...	...	...	...	35·4-36·2	Tsujimoto	44·2-47·1	Tsujimoto

As the commercial Japanese sardine oils sold hitherto were more or less mixed with other fish oils, the numbers placed against "Commercial Oils" in the tables of characteristics, p. 342, refer to oils the genuineness of which cannot be vouched for. The same strictures apply to the numbers given in the following table, due to *Fahrion* :—

	I. Iodine Value.	II. Acid Value.	III. Insoluble Acids + Unsaponifiable.	IV. Oxidised Acids. Per cent.	V. Unsaponifiable. Per cent.	VI. Fatty Acids freed from Oxidised Acids. Per cent.	VII. Molecular Weight of VI.	VIII. Neutralisation Value of the Fatty Acids freed from Oxidised Acids.[1]
Japanese fish oil, pale . .	164·0	10·8	95·52	1·16	0·52	93·84	282·8	185·8
,, brown . .	157·6	34·2	96·58	0·75	0·67	95·16	281·7	189·1
,, pale . .	135·7	12·3	97·04	0·41	0·82	95·81	295·7	181·4
,, reddish-brown	108·5	34·5	96·82	0·62	0·86	95·34	296·6	180·0
,, yellow . .	100·1	28·2	96·51	0·49	0·79	95·23	290·2	183·8

The following notes also refer to "Commercial Oil" :—

A sample of Japanese fish oil examined in the author's laboratory by *Walker* and *Warburton*[2] yielded 21-22 per cent of ether-insoluble brominated glycerides; the mixed fatty acids gave 23-23·3 per cent of an ether-insoluble bromide which became black at 200° C., without melting. Another sample of Japanese fish oil containing some liver oil, and deodorised on a large scale by a special process, yielded, in the bromide test, 49-53·3 per cent of brominated glycerides; its mixed fatty acids gave 38-39·3 per cent of a brominated product which turned black at 200° C., without melting.

Bull states that he has isolated from a number of Japanese fish oils 5·75-26·4 per cent of liquid fatty acids, absorbing 292·8-358·3 per cent of iodine.

Three specimens of undoubtedly pure Japanese sardine oils, free from other fish oils, were examined by *M. Tsujimoto*.[3] The characteristics obtained by him are recorded in the tables, p. 342. On brominating the mixed fatty acids 47·09, 44·24, and 44·88 per cent respectively of clupanodonic octobromide were obtained. Since 100 parts of the octobromide correspond to 30·16 parts of clupanodonic acid, the mixed fatty acids of Japanese sardine oil contain 13·34 to 14·20 per cent of clupanodonic acid.

Japanese fish oil must not be confounded with Japanese cod liver oil. Japanese fish oil is used in Europe in the leather industries, and for making soft soap.

[1] This number is termed by *Fahrion* "Inner saponification value."

[2] *Analyst*, 1902, 237.

[3] *Journ. of the College of Engineering, Tokyo Imperial University*, 1906, vol. iv. p. 1.

SARDINE OIL

French—*Huile de sardine.* German—*Sardinenöl.*
Italian—*Olio di sardine.*

This oil is obtained from *Clupea sardinus*, L., in the preparation of tinned sardines. The heads of the sardines are cut off, and the oil is expressed from the "scrap." Large quantities of this oil are prepared at the Spanish and French coasts. The oil recovered at the Spanish coast has been exported chiefly to Germany, ostensibly to be used in the manufacture of varnishes (see below).

Some characteristics of sardine oils, due to *Fahrion*, are given in the following table :—

	I. Iodine Value.	II. Acid Value.	III. Insoluble Acids + Unsaponifiable.	IV. Oxidised Acids. Per cent.	V. Unsaponifiable. Per cent.	VI. Fatty Acids freed from Oxidised Acids. Per cent.	VII. Molecular Weight of VI.	VIII. Neutralisation Value of the Fatty Acids freed from Oxidised Acids.[1]
Sardine oil, yellow . .	191·7	19·2	95·60	0·61	0·48	94·51	285·7	185·2
,, red . . .	167·9	21·7	96·55	1·35	1·01	94·19	297·7	177·2
,, reddish-yellow .	160·9	4·6	97·08	0·94	0·63	95·51	299·5	179·5

The solid fatty acids in a specimen of sardine oil examined by *Fahrion* were at first stated to consist of palmitic acid only; afterwards he modified this statement by allowing a small quantity of stearic acid, palmitic, however, preponderating. The liquid fatty acids did not contain physetoleic acid (Chap. III.), nor could oleic, linolic, or either of the two linolenic acids be detected. The unsaturated fatty acid was stated to be *jecoric acid*, $C_{18}H_{30}O_2$ (from *jecur*, liver; though sardine oil is not a liver oil), an isomeride of linolenic acid, but differing from it essentially in that it does not conform to *Hazura's* rule (Chap. III.). According to this rule it should yield, on oxidation with potassium permanganate in alkaline solution, a hexahydroxy acid, whereas it is apparently broken down with the formation of carbonic and volatile fatty acids. *Fahrion* considered this specimen of sardine oil to consist of 14·3 per cent of tripalmitin, and of 85·7 per cent of trijecorin.

These results have been severely criticised by *Weiss*,[2] and stand greatly in need of confirmation.

It has already been pointed out above that *Tsujimoto* could not detect any jecoric acid in Japanese sardine oil, and it may therefore be taken that neither does European sardine oil contain this acid. It seems most likely that also the European sardine oil contains clupanodonic acid. This could be readily proved by examining the behaviour of the brominated acids in the melting-point test.

Sardine oil is put to the same uses as Japanese sardine oil. The

[1] This number is termed by *Fahrion* "Inner saponification value."
[2] *Journ. Soc. Chem. Ind.* 1893, 937.

employment of the oil in the varnish industry can only be looked upon as an experiment which, doubtless, has led to failure.

HERRING OIL

French—*Huile de hareng.* German—*Heringsöl, Heringstran.*
Italian—*Olio di aringhe.*

For tables of characteristics see p. 346.

This oil is obtained from the several species of herring, *Clupea harengus* (North Sea), *C. pallasi*, C. and V. (Japan). Undoubtedly genuine samples of herring oil extracted from fish caught in Hokkaido, and prepared on a large scale in the same fashion as Japanese sardine oil (p. 341), were examined by *Tsujimoto*.[1] On standing, the Japanese herring oils deposited some "stearine."

The Japanese herring oils yielded on brominating 3·82 per cent and 6·54 per cent respectively of clupanodonic octobromide (see above). The unsaponifiable matter in the samples examined by *Bull* varied from 1·3 to 10·7 per cent, and the acid values from 1·8 to 40·2, whereas the Japanese herring oils examined by *Tsujimoto* had the acid values 2·02 to 10·42, and yielded from 0·87 to 1·1 per cent of unsaponifiable matter.

Herring oil, like all other fish oils, is largely used in the leather industry. *Procter* and *Holmes*[2] have ascertained the changes which fresh herring oil and "herring refuse oil" undergo on blowing with air for the number of hours stated in the table, at about 100° C.

Fresh Herring Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
0[3]	0·923	1·4780	145·0
3	0·923	1·4781	145·0
6	0·923	1·4784	141·0
9	0·926	1·4790	135·0
12	0·927	1·4795	133·0
15	0·930	1·4800	132·0
18	0·932	1·4805	130·0

Herring Refuse Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
0[3]	0·923	1·4784	146·0
3	0·923	1·4784	143·0
6	0·924	1·4785	142·0
9	0·925	1·4786	141·0
12	0·926	1·4790	138·0
15	0·927	1·4795	136·0
18	0·928	1·4795	132·0

[1] Tsujimoto, *Journ. College of Engineering, Tokyo Imperial University*, vol. iv. No. i., 1906.

[2] *Journ. Soc. Chem. Ind.* 1905, 1287.

[3] Original oil.

Physical and Chemical Characteristics of Herring Oil

	Specific Gravity.			Saponification Value.		Iodine Value.	
	°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
Clupea harengus . . .	15	0·9202-0·9391	Bull[1]	179-193·7	Bull.	131·0-142	Bull
						123·5	Fahrion
Clupea pallasi, C. and V. .	15·5	0·9178-0·9251	Tsujimoto	185·9-190·5	Tsujimoto	103·1-123·4	Tsujimoto

[1] Seven samples containing 10-13·3 per cent of liquid acids having iodine values from 289·3-319·8.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids +Unsaponifiable.		Melting Point.		Mean Molecular Weight.		Oxidised Acids.		Ether-insoluble Bromides.	
	Per cent.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
Clupea harengus .	95·64	Fahrion	...	...	291·9	Fahrion	1·59	Fahrion	...	...
Clupea pallasi . .	...	...	30-31·5	Tsujimoto	...	...	...	...	12·7-21·7	Tsujimoto

Oil.	German.	French.	[Mo]lecular [...]t of the [...]le Fatty [...]ids.	S[...] [...] Fa[...]
Stickleback .	Stichlingstran .	Huile de trois-épines	C[...] 7·4	
Whiting . .	Weissfischöl .	Huile de cyprin .	O[...]	
Sturgeon . .	Störtran . .	Huile d'esturgeon .	O[...]	
Sprat . .	Sprottenöl . . (Sprottentran)	Huile d'esprot, melet harenguet	O[...] 30	
Hoi[2] . .	Hoiöl . .	Huile de hoi . .		
,, . . .	...	...		
Carp . .	Karpfenöl . .	Huile de carpe .	O[...] ·7	
Cramp fish .	Zitterrochenöl .	Huile de torpille[5] .	O[...]	
Sun fish[1] . .	Mondfischöl .	Huile de mole de Méditerranée	O[...]	
Pilcher (Sardel)	Sardellenöl . .	Huile de pilchard .	O[...]	
Anchovy . .	Anchovistran .	Huile d'anchois .	O[...]	

[1] With regard to the liver oils see table facing p. 370.

[2] Norw[...]

[...]ion − 4° in 2[...]

[...]ahrungs- u.

SALMON OIL

French—*Huile de saumon.* German—*Lachsöl.*
Italian—*Olio di salmone.*

This oil is obtained on a very large scale from the salmon (*Salmo salar*, L.) as a by-product in the salmon preserving industry of British Columbia. The fish contains about 20 per cent of oil. The oil is pale golden-yellow, has a mild smell, and a tolerably pleasant taste.

The sample examined in the author's laboratory by *de Greiff*[1] gave the numbers recorded in the table of characteristics.

Physical and Chemical Characteristics of Salmon Oil

Specific Gravity at 15·5° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer.	
				°C.	"Degrees."
0·92586	182·8	161·42	0·55	25	78
				40	69·5

	Per cent.
Insoluble acids + Unsaponifiable . . .	95·02
Iodine value of the liquid fatty acids . .	197·4

The oil is imported in large quantities into this country, and is used in the leather and soap industries.

Lesser known fish oils, see table opposite.

β. Liver Oils

The liver oils contain notable amounts of cholesterol and other unsaponifiable substances. These bodies must be looked upon as the chromogenetic substances producing the colour reactions (especially when the oils are rancid), which were formerly considered as characteristic of liver oils. At present only the sulphuric acid colour test can be looked upon as having decisive importance; the blue colouration which *fresh* liver oils, in a solution of carbon bisulphide, give with conc. sulphuric acid is very distinct; if the oils are rancid a purple, or even dark brown colouration takes the place of the blue. Experiments carried out in my laboratory on a number of liver oils obtained from different fish, as also experiments by *Tichomirow* and *Kaiser*,[2]

[1] *Chem. Revue*, 1903, 223. [2] *Chem. Zeit.* 1895, Rep. 310.

confirm that this colour test is a general reaction for liver oils. The observation made by the author (Chap. VII.), viz., that some blubber oils also give the blue colouration in the sulphuric acid test, was explained by assuming an admixture with liver oil. *Thomson* and *Dunlop* have, however, recently stated that a seal oil of undoubted purity, as also a genuine porpoise oil, showed the blue violet colouration with concentrated sulphuric acid.

The *intensity* of the phospho-molybdic acid test (Chap. VII.) is also characteristic. If the chloroformic solution of a liver oil, after shaking with the phospho-molybdic acid reagent, be allowed to stand, there is formed a blue ring at the zone of contact of the two layers, no doubt due to the neutralising action of the bases in the oil. In this form the phospho-molybdic test may serve to identify a liver oil. Rancid liver oils, however, do not give a distinct colour reaction. Whereas the sulphuric acid test, as a rule, indicates liver oil, the phospho-molybdic acid test must not be looked upon as having the same importance for discriminative purposes.

COD LIVER OIL

French—*Huile de foie de morue.* German—*Dorschleberöl, Leberöl.*[1]
Italian—*Olio di fegato di merluzzo.*

For tables of characteristics see pp. 354, 355.

Genuine cod liver oil is obtained from the liver of the cod, *Gadus morrhua* (and of the dorsch, the young of *G. morrhua*, formerly considered a separate species, *Gadus callarias*).

The habitat of the cod is not yet known precisely, yet annually at certain times enormous shoals of cod frequent the coast of the northern seas, chiefly the coasts of Norway, Scotland (Iceland), the east coast of Canada and of the United States, as also the west coast of the United States and the coasts of Japan and Siberia. The best known and oldest fishing-grounds are those of Norway, where the fish makes its appearance at regular intervals of the year. Thus in the Lofotes the cod appears in February, and the fishing season lasts from February till April. Then the cod makes its appearance at Finmarken in June; but here the fish seem to arrive in a still immature form, and hence do not yield as much oil as on the Lofoten coast. Moreover, the cod frequenting the Finmarken coast is accompanied by other fish, whose livers naturally become mixed with those of the cod. Hence the Finmarken cod liver oil is not considered of the same high quality as the Lofoten oil. The chief object of the cod fishing industry was, of course, to "cure" the fish after cleaning it,

[1] The German term "Kabeljauleberöl" should not be applied to cod liver oil, but should be reserved for haddock liver oil (see table facing p. 370).

the livers being thrown away together with the most putrescible parts of the fish, which permitted of no curing. No doubt the manufacture of cod liver oil was due to the accidental discovery that from the heaped-up livers an oil exuded, which was found to possess medicinal properties. Since then the cod liver oil industry has assumed considerable dimensions, as may be gathered from the fact that in 1905 41,907 hectolitres of medicinal oil (and 12,960 hectolitres of cod oil), and in 1906, 42,908 hl. of steam cod liver oil, were produced in Norway.

The following table shows the variations in the production of cod liver oil in the Lofoten Islands during the last twenty-one years.[1] The numbers given for March and April include the production of the previous months :—

Production of Medicinal Cod Liver Oil in the Lofoten Islands

Year.	January-February.	March.	April.	Equivalent in Barrels.
	Hect.	Hect.	Hect.	
1886	2990	9,329	10,000	8,620
1887	753	8,044	9,500	8,169
1888	3442	15,057	16,100	13,879
1889	655	7,933	12,900	11,120
1890	2261	14,340	16,700	14,396
1891	420	13,570	19,600	16,896
1892	1970	6,600	7,920	6,828
1893	3178	15,528	18,550	15,992
1894	1993	8,160	12,231	10,544
1895	845	10,700	12,300	10,604
1896	400	6,240	8,850	7,629
1897	2336	11,000	18,260	15,741
1898	600	6,510	11,254	9,702
1899	1934	11,299	18,450	15,906
1900	1301	7,965	10,752	9,269
1901	1592	12,051	15,889	13,697
1902	634	7,768	9,628	8,300
1903	...	252	614	529
1904	...	833	2,690	2,319
1905	374	6,183	11,493	9,909
1906	3232	12,974	16,952	14,614

In Newfoundland and at the coast of Labrador the cured fish was also the main product, and the liver oil industry has only gradually assumed the proportions it possesses to-day. The chief attention having been paid to the fish, the cod liver oil industry has lagged behind that of Norway as regards medicinal cod liver oil, although the nearness of the fishing-grounds to the rendering establishments permitted, at an early stage of the cod oil industry, the production of commercial *cod oil* of a better quality than could be obtained in this country (see below). During the last few years the cod fish industry

[1] Bousfield, *Chemist and Druggist*, 1907, 207.

has assumed enormous dimensions on the Pacific coast, especially so on the Pacific coast of America, and bids fair to surpass in dimensions the great industry of the east coast of the United States. Up to a few years ago San Francisco was the greatest cod fish centre of the Pacific coast, the fishing vessels, which exploited chiefly the fishing-grounds near the Shumagin Island on the south of Alaska, bringing their cargoes to San Francisco. Recently enormous rendering establishments have been erected at Anacortes in Puget Sound, and also at Vancouver. (In British Columbia hitherto little attention has been paid to the cod industry, as the chief interest was centred in the catch of salmon and halibut.) All establishments in the three curing stations named, send out fishing flotillas to the south of Alaska. At present the manufacture of medicinal cod liver oil plays an unimportant part on the west coast of America, as the amount of detailed attention required in the production of the best qualities is still wanting.

Latterly Japan has also entered the lists as a manufacturer of cod liver oil, both medicinal and commercial. The enormous fishing-grounds in the Okhotsk sea, where cod is most plentiful, have been leased to the Japanese, and a large production of both medicinal oil, as also commercial cod oil, may be expected in the near future.

In order to illustrate by a few figures the extent of the cod industry, and indirectly that of the cod liver oil, it may be stated that the value of the total cod fishing of North America in 1905 was placed at £2,500,000. The large increase that takes place from year to year may be gathered from the fact that, whereas in 1904 the weight of cod caught on the Pacific coast was 10,204,000 lbs. (3,642,000 fish), it had reached in 1905, 14,568,000 lbs.

The fish is caught either by hook and line, or in nets (cod traps). The latter method is extensively used where the fish can be driven into narrow fjords, as *e.g.* in Norway. It is said that the fish caught in net is fatter, and yields therefore a larger liver and more oil, than the fish caught by hook and line. The head of the fish is severed from the body, the fish split along the abdomen, and the liver thrown out by the operator by a rapid jerk.

In the early years of the manufacture of cod liver oil the livers were heaped up in barrels and allowed to undergo a process of spontaneous putrefaction, whereby the liver cells burst and the oil exuded. The oil so obtained was contaminated with decomposition products of the liver, and therefore possessed a rank odour and nauseous taste, with which even nowadays popular prejudice associates medicinal cod liver oil. With the increased facilities of intercourse between the cod fishing stations and properly equipped rendering establishments, this exceedingly crude process of manufacture underwent considerable improvements. The livers were then properly sorted and washed as rapidly as possible, so as to inhibit the spontaneous decay, which sets in on exposure of the livers to the air. Moreover, the oil exuding from the livers was collected in fractions, as it were, and thus graded, the oil running out at first, as the best, being kept

separate from the oils obtained from the livers in a more advanced state of decomposition.

Thus up to a few years ago the following three qualities of cod liver oil, as obtained by the natural decay of the livers (in the Lofoten Islands), were known in commerce: (1) pale cod liver oil, (2) light brown oil, (3) brown oil.

Pale cod liver oil[1] and *light brown oil* are used in pharmacy. The former is the first product, the light brown oil forming the second product, after the disintegration of the livers has proceeded further.

The *brown oil* was that obtained from the livers which had reached a very advanced state of decay, and had actually become putrid. This oil was recovered by boiling the putrid livers with water, skimming off the oil, and finally pressing the scrap (see below).

Even the following four qualities of cod liver oil, which were differentiated by *P. Moeller*,[2] viz. (1) *raw medicinal*, (2) *pale oil*, (3) *light brown oil*, (4) *brown oil*, are no longer recognised in the trade. Besides, so little was obtained of the raw medicinal oil, that it did not pay to collect it separately.

During latter years the manufacturing processes of cod liver oil, especially those of medicinal oil, have undergone a complete change, chiefly in consequence of the erection of properly equipped establishments in the Lofotes by English pharmacists. The demand for pure medicinal cod liver oil had already forced some pharmacists in this country to prepare the medicinal oil themselves, by heating absolutely fresh livers, taken from fish brought to shore alive, in jacketed vessels heated by hot water or by steam. Under the action of the high temperature the cell membranes burst, and the oil exuded. The best medicinal oil—termed "steam liver oil"—was thus obtained. This method was taken up by cod oil extractors in Hull, Aberdeen, Dundee, etc., and finally transferred to the above-mentioned rendering establishments in the Lofotes. The best medicinal oil is manufactured there on the lines sketched for the manufacture of "steam liver oil." The livers are worked up immediately after being taken from the fish so as to avoid exposure to the air, it having been found as an invariable rule that even exposure for a few hours was apt to deteriorate the quality of the oil. This process, taken as it were from the laboratory, was found too cumbersome and too slow, since the extraction of the oil from the livers required several hours. At present, in the best equipped establishments in Norway, the fresh livers are placed (almost immediately after they have been taken from the fish, washed and sorted—all livers showing stains being discarded) in tin-lined vessels provided with open steam coils. Low-pressure steam is then blown into the livers, and the oil exudes almost immediately.

[1] The pale yellow colour is due, according to P. Moeller, to a pigment (lipochrome) which is destroyed by the action of bright light ("sun-bleached oils").

[2] Moeller, *Cod Liver Oil and Chemistry*, London, 1895, where complete details as to the old processes of manufacturing cod liver oils in Norway are given.

The best qualities of crude medicinal oil are prepared in this manner. Previously the Norwegian medicinal oil was looked upon as the best brand in the market, no doubt owing to the fact that in former years the nearness of the fishing stations to the rendering establishment, and the careful sorting of the livers, secured the best oil that could be produced under the then ruling circumstances. Although the conditions favouring the immediate working up of the livers also prevail in Newfoundland, the details of the manufacturing operations were formerly not carried out with such care as to secure an equally good oil. Hence the Newfoundland oil was considered as much inferior to the best Norwegian medicinal oil. At present, however, the most modern methods of manufacture have been introduced also in Newfoundland. Since the Newfoundland manufacturers have adopted the packages used by the Norwegian makers and abandoned wood, which was always apt to impart an undesirable flavour to the oil, Newfoundland medicinal cod liver oil can hardly be considered as inferior to Norwegian oil. Therefore, it is to be expected that the demand for oil of unobjectionable taste will entirely do away with antiquated methods, and that the manufacture of "pale cod liver oil" and "light brown oil," obtained from naturally *decayed* livers, will die out completely.

The medicinal oils in the market, prepared by the processes sketched above, are of such excellence that it would hardly appear necessary to have recourse to more elaborate details, such as the extraction of the oil in a vacuum pan,[1] or in a current of carbonic acid.

The crude medicinal cod liver oil is filtered to free it from liver tissue, and bleached by treatment with fuller's earth, or by exposure, in closed glass vessels, to the action of sunlight. Medicinal oil so prepared deposits "stearine" at a low temperature, and such oil is termed "congealing oil." Some Pharmacopœias, such as the British Pharmacopœia, prescribe a "non-congealing" oil, *i.e.* an oil which will not set at the freezing point. Such medicinal oil is obtained by allowing the crude medicinal oil to cool down to below 0° C., and filtering it at a temperature of −10° C. The "stearine" is sold as "fish stearine" of best quality, for soap-making purposes.

All unsound livers, and those which have been exposed for a shorter or longer time to the atmosphere, would then be worked up solely for "brown oil." This brown oil, if prepared exclusively from cod livers,—the "cod oil" of commerce,—is, of course, a genuine cod liver oil. Before steamers were introduced into the cod fishing industry off the coast of Great Britain, the fishing boats were sometimes for a week on the fishing-grounds, and the fish could not be brought to shore alive. The livers were collected, and thus they were landed in a more or less putrid state. The gases which collected in the barrels, in consequence of the high state of putrefaction, sometimes exerted so high a pressure that the ends of the barrels—as the author has witnessed himself—were driven out. The fresher the

[1] Harrison, Wild, Robb, English patent 25,683, 1904.

livers were, the better was the oil. For this reason "Newfoundland cod oil," in consequence of the nearness of the fishing station to the rendering establishment, was the best class of commercial cod oil. Next to this came the "Norwegian cod oil," which commanded a higher price than the English cod oil. The author proved on a large scale that the preference given to the Norwegian fish oil was solely due to the greater freshness of the oil. The English oil, having undergone oxidation, required a special process of purification in order to bring it into line with the Newfoundland quality. In consequence of the displacement of sailing craft by steamers, the livers are now brought to shore,[1] even in this country, in a much fresher state than formerly; hence the quality of cod oil manufactured in this country has greatly improved during the last few years.

In the manufacture of cod oil, the livers are boiled out with water, when the oil which rises to the top is skimmed off. The scrap ("foots") is pressed in hydraulic presses to yield a further quantity of oil which is of much inferior quality. The expressed "scrap" is then worked up into "fish manure."

The crude cod oil, termed "unracked" cod oil, contains a considerable quantity of "stearine," which separates out on cooling. This "stearine" is recovered either by filtering, or by merely drawing it off from the bottom of the tanks, in which the crude cod oil has been allowed to stand for some time, exposed to cold. The "stearine" so obtained is sold for soap-making purposes, as a lower kind of "fish stearine" than that obtained from good medicinal oil, or as "fish tallow" for currying.

The commercial "Coast cod oil" is a liver oil obtained from other fish besides cod, such as hake (*Merluccius vulgaris*), haddock (*Merluccius æglefinus*), ling (*Molva vulgaris*), coal fish (*Gadus merlangus*, s. *carbonarius*, *virens*), in fact any fish that is caught in the nets of the trawlers in the open sea. The livers from these fish are collected in barrels, and usually reach the works of the cod oil extractor in a more or less putrid state, depending on the time that has elapsed since the fish has been caught.

The colour of pure medicinal oil is pale yellow or light yellow. The best qualities have only a slight fishy odour, and a not unpleasant taste. The lower qualities of cod liver oil, such as represented by cod oil, vary in colour from dark yellow down to almost black. The oil expressed from the "foots" is generally of a black colour, and has a rank, fishy odour.

According to the temperature at which the oil is recovered it contains varying quantities of "stearine." On standing at the ordinary temperature the bulk of the "stearine" settles out. Cod liver oils freed from "stearine" are known as non-congealing (non-freezing) or "racked" oils (cp. "Demargarinated Oils," Chap. XV.); therefore the solidifying points of commercial samples vary considerably.

[1] Hence the patented appliances (Johnson, English patent 26,728, 1902) for rendering on board trawlers would appear superfluous at present.

Physical and Chemical Characteristics of Cod Liver Oil (chiefly *medicinal oil*)

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Maumené Test.		Refractive Index.		
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	° C.	Observer.	At ° C.		Observer.
15	0·922-0·927	Kremel [1]	0 to −10	Salkowski	182-187	Allen	158·7-166·6	Thomson and Ballantyne	0·40-0·45	Lewkowitsch	116	Baynes	15	1·4800-1·4852	Strohmer
,,	0·9247	Bull [2]			182-188	Lewkowitsch		Parry	0·55-0·76	Parry	113	Allen	15·5	1·4783-1·4814	Tolman [10]
,,	0·9326	,, [3]			185·1-191·4	Thomson and Ballantyne	159-168·5	Lewkowitsch					20	1·4769-1·4800	Utz
,,	0·9232-0·9252	,, [4]					135 [11]	,,					20	1·4785-1·4825	Harvey
,,	0·9217-0·9256	,, [5]			179-193·4	Parry and Sage					Specific Temperature Reaction.		60	1·4621	Thoerner
,,	0·9310-0·9410	,, [6]			183-188 [1]	Bull	166-198·1	Bull					Oleo-refractometer.		
15·5	0·923-0·930	Lewkowitsch			179·0 [5]	,,	135-140·8 [3]	,,					"Degrees."		Observer.
,,	0·9249-0·9265	Thomson and Ballantyne			168·3-175·2 [6]	,,	159·7	Harvey [7]			243-272	Thomson and Ballantyne	+38 to +53		Jean
20	0·9202-0·9246	Wijs [9]					176·9	,,					+40 to +46 at 22° C.		Pearmain
99 (water 15·5 = 1)	0·8742	Allen					154·5	Wijs					+43·5 to +45 at 22° C.		Dowzard [8]
15·5	0·9259-0·9291	Parry					181·3	Lewkowitsch [12]					+40·3 to +48		Lewkowitsch [16]
,, (water 15·5 = 1)	0·9224-0·9270	Tolman [10]					165·9	,, [13]					Butyro-refractometer.		
25 (water 25 = 1)	0·9174-0·9220	,, [10]					169·7	,,					At ° C.		Observer.
							176·9	Tolman [10]					15	81·3-86·7	Utz
							135·4-172·6						20	77·5-83·2	,,
													25	75	Mansfeld
													40	71	,,
													25	78 ; 79 [14]	Lewkowitsch
													40	68·5 ; 70·5	,,
													25	77-80 [13]	,,
													40	68-71	,,
													25	75 [15]	,,
													40	66	,,

[1] Medicinal oil. [2] Steam liver oil, Lofotes. [3] Japanese steam liver oil, medicinal. [4] Pale oil. [5] Light brown oil.
[6] Brown oil. [7] *Journ. Soc. Chem. Ind.* 1902, 694. [8] *Pharmac. Journ. Transact.* (4), 6, 532.
[9] Thirty-four samples of pure cod liver oils of different qualities (*Zeit. angew. Chem.* 1902, 1192). [10] American cod liver oils, *Journ. Amer. Chem. Soc.* 1906, 391.
[11] Containing "stearine." [12] Newfoundland, freed from stearine. [13] Norwegian, freed from stearine. [14] Three samples. [15] Not stearine free. [16] Season 1907.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Kind of Oil.	Solidifying Point.		Melting Point of *Solid* Fatty Acids.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.		° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
			Titer Test.											
95·3[1]	Lewkowitsch	Medicinal . .	17·5-18·4	Lewkowitsch	22-25	Parry	204·4	Dieterich	287-290	Parry	164-171	Parry	1·4521	Thoerner
96·5[1]	Fahrion	Coast cod . . .	18·7-19·3	,,			207	Thoerner						
		Norwegian . .	13·3-13·9	,,										
		Dark, unracked .	22·5-24·3	,,										

[1] Medicinal oil.

The chemical composition of the cod liver oil glycerides appears to be very complicated. Since palmitic and stearic acids have been isolated, the occurrence of palmitin and stearin must be accepted as proven. The "stearine" separating from cod liver oil on cooling contains, however, but little true "stearine," *i.e.* glycerides of stearic and palmitic acids. Samples of cod liver oil stearine examined in my laboratory had iodine values ranging from 94 to 102. *Heyerdahl* (evidently in a less carefully prepared specimen) found 113·4. On a large scale the author obtained from a cod oil having the iodine value 170·6 a softish "stearine" of the iodine value 116·7, whereas the liquid portion had the iodine value 178·0. By pressing the "stearine" a hard cake was obtained of the melting point 37·8° C., and of the iodine value 102·4.

Small quantities of glycerides of the lower saturated fatty acids, such as the glycerides of acetic, butyric, valeric, and capric acids, have been stated by various authors to occur in cod liver oil. The volatile fatty acids are, however, secondary products due to the putrefaction of livers, which in the older processes of manufacture always occurred to some extent. The best medicinal liver oils prepared by steam are free from volatile acids (see below).

The nature of the liquid fatty acids in cod liver oil is but imperfectly understood as yet; their high iodine value points to the presence of large proportions of less saturated acids than those belonging to the oleic series. *Fahrion*,[1] examining the liquid fatty acids from a cod liver oil absorbing 175·5 per cent of iodine, could not identify jecoric acid with certainty. *Fahrion* assumes the presence of an acid, $C_{17}H_{32}O_2$, termed asellic acid (see Chap. III.). He could not detect physetoleic acid (iodine value = 100), stated by some writers to form the chief constituent of cod liver oil. *Heyerdahl*[2] concluded that the mixed fatty acids of cod liver oil, freed from its "stearine," contained, amongst other hitherto not identified acids, about 4 per cent of palmitic acid, 20 per cent of jecoleic acid (Chap. III.), and 20 per cent of therapic acid (Chap. III.). The presence of jecoleic acid is inferred from the existence of dihydroxyjecoleic acid (prepared by the oxidation of the mixed fatty acids with potassium permanganate), and that of therapic acid from the octobromide $C_{17}H_{26}Br_8O_2$ obtained on brominating the liquid fatty acids. No oleic acid was found in cod liver oil; the "stearine," no doubt, contains some unknown unsaturated acid or acids. In the fresh state cod liver oil is free from hydroxylated acids.

An approximately accurate method for the resolution of the liquid cod liver oil fatty acids consists, according to *Bull*,[3] in the fractional separation of their alkali salts. Cod liver oil is saponified with double normal anhydrous alcoholic potash, and the potassium salts obtained on concentrating the solution are carefully pressed after cooling. The pressed cake is recrystallised from alcohol and pressed again, and the united mother liquors are concentrated, cooled, and pressed, these

[1] *Journ. Soc. Chem. Ind.* 1893, 935. [2] *Cod Liver Oil and Chemistry*, p. lxxxix.
[3] *Chem. Zeit.* 1899, 996.

operations being repeated until a solid potassium salt is no longer obtained. The mother liquors are converted into the sodium salts by isolating the free fatty acids and neutralising them with anhydrous alcoholic soda. The sodium salts are purified in exactly the same manner as described for the potassium salts. The free fatty acids are recovered from the solid salts thus obtained, by dissolving the soaps in water in a current of steam, and gradually allowing hydrochloric acid to run on to them, until the solution is distinctly acid. From the alcoholic mother liquors the alcohol is completely removed by distilling *in vacuo*. The residue is then thoroughly exhausted with dry ether. Thus the sodium salts of the most unsaturated acids, as also cholesterol, are dissolved. The soaps are recovered from the ethereal solution by washing with water. The ether-insoluble soaps are dissolved in absolute alcohol; by allowing to crystallise, a small amount of a sodium salt may be recovered from the remaining alcoholic mother liquor. The alcohol is finally removed by evaporation and the fatty acids are liberated. Thus the following four groups of fatty acids were obtained :—

A. Fatty acids, the potassium salts of which crystallise from alcohol.
B. Fatty acids, the sodium salts of which crystallise from alcohol.
C. Fatty acids, the sodium salts of which are readily soluble in ether.
D. The remaining fatty acids.

From 1000 grams of cod liver oil *Bull* obtained the following quantities of acids :—

Fatty Acids.	Weight.	Neutralisation Value.	Iodine Value.
A.	334 grams	194·2	67·5
B.	375 ,,	190	135·6
C.	120 ,,	167	322·4
D.	69 ,,	169	347

For the conclusions which *Bull* draws from his experiments and for the analytical methods he recommends (all of which stand greatly in need of confirmation [1]), the reader must be referred to the original paper.

On brominating cod liver oil, *Hehner* and *Mitchell* obtained 56·23 per cent of brominated glycerides, to which they ascribed the hypothetical formula, $C_3H_5(C_{18}H_{29}O_2Br_6)(C_{18}H_{29}O_2Br_6)(C_{18}H_{33}O_2Br_2)$. *Walker* and *Warburton* found in the author's laboratory only 33·7-35·3 per cent of brominated glycerides. From a commercial cod oil, *Hehner*

[1] *Jahrbuch der Chemie*, x. 386.

and *Mitchell* obtained 35·5 per cent of brominated glycerides, *Walker* and *Warburton* 30·6-32·7 per cent. The mixed fatty acids of a cod liver oil yielded to *Hehner* and *Mitchell* 18 per cent of a bromide containing 62·91 per cent of bromine (theory requiring for a hexabromo compound 63·31 per cent of bromine). *Walker* and *Warburton*, again, obtained from a genuine cod liver oil, which gave 33·7-35·3 per cent of brominated glycerides, 29·8-30·4 per cent of brominated fatty acids. The proportion of bromo compounds no doubt depends on the state of freshness of the sample under examination.

The foregoing notes would appear to show that fatty acids of the series $C_nH_{2n-6}O_2$ may be present in cod liver oil. An acid or acids (if any) having this composition must, however, differ from linolenic acid, since the isolated bromo compounds of the fatty acids do not melt, like linolenic hexabromide, at about 175° C., but remain apparently unchanged until a temperature of 200° C. is reached, when they are converted into a black mass, without, however, melting to a clear liquid. The difference between the unsaturated acid (or acids) of cod liver oil and the unsaturated acids of the vegetable drying oils is further exemplified by the fact that cod liver oil does not dry to a skin like the vegetable drying oils.

From the latest researches of *Tsujimoto* we must conclude that acids of the formula $C_nH_{2n-8}O_2$ which yield octobromides on treating with bromine occur also in cod liver oil. *Heyerdahl* appears to have been the first to prove the presence of an octobromide, but it should be pointed out that the formula of the "therapic acid" differs from that of *Tsujimoto's* clupanodonic acid, the occurrence of which has been proved so far in fish and whale oils.

Recently *Bull*[1] examined the methylesters of cod liver oil fatty acids (cp. Chap. XII.), obtained by treating cod liver oil with sodium methylate. By subjecting the esters to fractional distillation *in vacuo* at 10 mm. pressure, three main fractions were obtained, boiling at 186° C., 206° C., and 224° C. respectively. In the following table the main results of this investigation are summarised :—

Fraction boiling from	Contains
161·5 to 165° C.	Myristic acid
185 ,, 186° C.	Palmitic acid, palmitoleic acid[2]
200 ,, 206° C.	Stearic acid, oleic acid
223 ,, 225° C.	Gadoleic acid[3]
239 ,, 240° C.	Erucic acid[4]

Although *Bull* distinctly mentions that acids occur in cod liver oil having very high iodine values, he appears to have overlooked those fatty acids which occur in considerable quantity in cod liver oil,[1] and yield highly brominated acids. Hence *Bull's* statement that *Heyerdahl's* jecoleic acid does not exist, and that the latter's dihydroxyjecoleic acid is possibly a eutectic mixture of dihydroxy-

[1] *Berichte*, 1906, 3570.

[2] Bull did not name this acid ; I suggest for it the name "palmitoleic acid."

[3] Cp. Vol. I. Chap. III. [4] Cp. p. 334.

stearic acid and dihydroxygadoleic acid, must also be accepted with reserve.

The occurrence of morrhuic acid $C_9H_{18}NO_3$ (differing from tyrosine by H_2) in cod liver oil requires confirmation.

On reducing cod liver oil with hydrogen in the presence of colloidal palladium in the cold, *Paal* and *Roth*[1] obtained a solid fat softening at 43° C. and liquefying at 45° C. The iodine value of the reduced glyceride was 3, whereas the original oil absorbed 135·8 per cent of iodine (Cp. Vol. I. Chap. I.).

A characteristic constituent of cod liver oil is **cholesterol.** This is isolated by preparing the unsaponifiable matter in the usual manner and recrystallising it from alcohol, when the characteristic cholesterol crystals are deposited. *Salkowski*[2] gives as the average of cholesterol obtainable from medicinal cod liver oils 0·3 per cent. The laevo-rotation of the plane of polarised light exercised by cod liver oil is undoubtedly due to the presence of the cholesterol. *Dunlop* and *Thomson* found the specific rotatory power of several cod liver oils $[\alpha]j = -0{\cdot}26°$.

The somewhat considerable amount of cholesterol which was found in the oils manufactured two or three decades ago, has led to the assumption that the slight optical activity which some high boiling mineral oils from petroleum exhibit (see Vol. III. Chap. XV.), was due to the content of cholesterol in those fish and liver oils, which are assumed to be the mother substances of the natural petroleums.[3]

Besides cholesterol, the unsaponifiable matter of cod liver oil contains "lipochromes" to which the colour reactions, which have formerly played so important a part in the examination and identification of cod liver oil (see below), are due. *Gautier* and *Mourgues* state that they have isolated from the unsaponifiable matter a substance similar to lecithin, inasmuch as it yielded phosphoric acid, glycerol, and a fatty acid, termed by them morrhuic acid (see above); it has been pointed out already that the existence of this acid is very doubtful.

In the older literature on this subject there are recorded many statements as to the occurrence of bases which were, of course, found in the unsaponifiable matter. Undoubtedly most of these bases are secondary products, due to the decomposition the livers underwent whilst the oil exuded from them spontaneously. Thus, *Heyerdahl* found in raw medicinal oil, *i.e.* first oil which exuded spontaneously from livers by natural decay, small quantities of ptomaines; and *Gautier* and *Mourgues*[4] before him found organic bases in "light brown" cod liver oil to the extent of from 0·035 to 0·050 per cent. They isolated the following bases:—

(*a*) *Volatile:* butylamine, isoamylamine, hexylamine, dihydrolutidine.

(*b*) *Non-volatile:* morrhuine $C_{19}H_{27}N_3$, aselline $C_{25}H_{32}N_4$.

[1] *Berichte*, 1908, 2283. [2] *Zeit. f. analyt. Chem.* 26, 565.
[3] See Lewkowitsch, *Jahrb. der Chemie*, xvii. p. 417.
[4] *Comptes rend.* 107, 254; 626; 740.

Recently *Philip B. Hawk*[1] isolated from "light amber," "light brown," and "dark brown" oils 0·106, 0·117, and 1·09 per cent respectively of "leucomaïnes," by the method of *Gautier* and *Mourgues*. By fractional distillation butylamine, amylamine, hexamyline, and dihydrolutidine were separated. In the non-volatile portion morrhuine was identified, but not the aselline, described by *Gautier* and *Mourgues*.

Heyerdahl has isolated trimethylamine by means of its platinochloride. This base, however, like those mentioned above, must be considered as a product of decomposition of the cellular tissue of the livers. Biliary colouring matters, stated to occur by earlier observers, are absent. According to *Salkowski* the colouring principle in cod liver oil belongs to the class of *lipochromes*.

To most of these bases in turn have been ascribed the medicinal properties of cod liver oil, but there seems to be no doubt that all these bases are secondary products derived from the decayed cellular matter of the livers. The best medicinal cod liver oils, *i.e.* those oils which have been prepared from fresh livers by steaming, do not contain these bases (which impart the nauseous taste to the oils obtained by the natural decay of livers). Even the amount of lipochromes and other unknown substances, such as biliary colouring matters, the presence of which is indicated by the characteristic violet colour reaction of liver oils (see p. 365 below), has decreased considerably with the improvements in the production of this oil. Indeed the author is of the opinion, derived from the examination of a very large number of medicinal oils of various origins, that the fainter is the blue colour reaction with concentrated sulphuric acid the better is the taste of the oil, for the colour reaction is merely indicative of impurities which can be kept out of a properly manufactured article. It therefore follows that the statement, still occurring in the pharmaceutical literature, that a strong colour reaction indicates biliary substances (which were said to constitute the therapeutical effect of cod liver oil) is valueless. The same strictures apply to statements as to the occurrence of albuminoid substances, some of which were credited with the power of combining chemically with iron, manganese, calcium, magnesium, and sodium.

By some writers the *therapeutic value* of cod liver oil was ascribed to the small amount of iodine it contained (therefore cod liver oils are met with to which iodine or potassium iodide has been added fraudulently). The following amounts of iodine have been recorded :—

[1] *Proceedings, American Physiological Society*, 1907-8, xxii. ; *Americ. Journal of Physiology*, vol. xxi. (1908), No. 11.

[TABLE

Proportion of Iodine in Cod Liver Oil

Description of Oil.	Iodine.	Observer.
	Per cent.	
Pale . . .	0·020	Andrès
Yellow . . .	0·031	,,
...	0·00138-0·00434	Stanford
...	0·0002	Heyerdahl

In the opinion of the author the medicinal effect of cod liver oil, however, must rather be looked for in the facility with which it is hydrolysed or digested, and it cannot be doubted that this property is caused by the peculiar constitution of its unsaturated fatty acids. From the medicinal point of view, that cod liver oil is the best which has been prepared from fresh livers and kept protected from the action of light and air.

Heyerdahl has studied the influence which the length of time during which the livers are heated has on the proportion of free fatty acids in the oil produced. He found, contrary to expectation, that the percentage of free fatty acids decreased slightly but perceptibly as the time of heating was increased (from 20 to 80 minutes) and the temperature was allowed to rise (from 62° to 85° C.). This result may be ascribed to the volatilisation of free volatile acids at the higher temperature, or to the fact that the first portions of the extracted oil were richer in fatty acids, or to both causes conjointly, or to the fact that enzymes causing hydrolysis (see "Lard") were destroyed by heating. Experiments, in which measured volumes of air were driven through samples of oil heated in the water-bath, proved that the free fatty acids decreased up to a certain point, and then slowly rose to, or beyond, the original percentage. The proportions of free fatty acids never exceeded 0·69 per cent, calculated as oleic acid.

The oil obtained by passing steam directly into the livers is practically devoid of volatile fatty acids; their occurrence in commercial oils must therefore be due to some secondary process. This statement has been corroborated by the examination of liver oils from other species of fish (*Heyerdahl*).

In the examination of *Medicinal Cod Liver Oil* the organoleptic methods must be applied in the first instance. A good medicinal oil should be of pale colour, and should have a mild fishy taste, and possess only a slight fishy odour. The taste alone is able to indicate whether the amount of free fatty acids is too high, and whether any decomposition products of the liver tissue have passed into the oil.

The *chemical* tests which furnish the most important indications for the valuation of medicinal cod liver oil comprise the *acid value*, the *iodine value*, and the *Reichert value* (*Reichert-Meissl value*).

The proportion of *free fatty acids* should be as small as possible. No definite limit can be laid down, but a comparison with the numbers recorded in the following table will afford the necessary guidance :—

Free Fatty Acids in Cod Liver Oils, calculated as Oleic Acid

Description of Oil.	Colour.	Free Fatty Acids.	Observer.
		Per cent.	
Raw medicinal oil . .	Pale	3·79	Heyerdahl
,, ,, . .	Somewhat darker	3·87	,,
,, ,, . .	Darkest	3·96	,,
Medicinal oil . . .	Yellow	0·36	Thomson and Ballantyne
Medicinal oils . . .	...	0·34-0·60	Parry and Sage
,, ,, . . .	...	0·12-0·48	Lewkowitsch
,, ,, . . .	...	0·43-1·01	Parry

It may therefore suffice to state that the best steam cod liver oils contain from 0·3 to 1·5 per cent of free fatty acids (calculated to oleic acid), whereas medicinal oil prepared by older processes exceeds this number, and may reach as much as 3 or even more per cent.

The *Reichert value* should be low. Good medicinal oils show *Reichert* numbers lying below 0·5. A higher number, especially one exceeding 1·0, would indicate that the livers employed for the extraction of the oil have not been perfectly fresh; such oil would also betray its high amount of volatile acids by an inferior taste.

The higher the *iodine value*, the less oxidation can have taken place, and if the medicinal properties be valued by the amount of unsaturated fatty acids, then, *cæteris paribus*, the higher the iodine value the better the oil. It will be gathered from the table of characteristics that the author found (in a cod liver oil used for feeding calves) the high number 198·1. The mean iodine value of a good medicinal non-congealing oil may be taken as 167. Since, however, the magnitude of the iodine value depends on the extent to which the "stearine" has been removed, it would not be permissible, without further examination, to declare samples having lower iodine values as adulterated.

The amount of *unsaponifiable matter* should not as a rule exceed 1·5 per cent (cp. table, p. 363). Larger amounts would point (in the absence of mineral oils) to admixture with other liver oils such as shark liver oil, which contains notable proportions of spermaceti, or of liver oil from *Merlangus* (Sej liver oil, saith oil), which has been frequently substituted for cod liver oil.

Inferior cod liver oils which have a higher proportion of unsaponifiable matter should be rejected as indicating badly prepared oil. Thus Japanese cod liver oil, which has not yet been prepared according to the best methods, contains amounts of unsaponifiable matter exceeding 2 per cent.

A comparison of the amounts of unsaponifiable matter contained in best cod liver oils with those found in oils of low quality is afforded by the following table :—

Unsaponifiable Matter in Cod Liver Oils

Description of Oil.	Colour.	Unsaponifiable.	Observer.
		Per cent.	
Medicinal cod liver oil . .	Reddish yellow	0·54	Fahrion
,, ,, . .	Yellow	1·08	,,
,, ,, . .	Pale yellow	1·44	,,
,, ,, . .	Yellow	0·87	Thomson and Ballantyne
Steam cod liver oil, medicinal .	Pale yellow	0·61	Fahrion[1]
,, ,, ,,	Almost colourless	0·64	,,
,, ,, ,,	Pale yellow	0·98	,,
,, ,, ,,	Pale yellow	0·6-1·68	Lewkowitsch
,, ,, of rank odour	...	2·4-4·6	Parry
,, ,, Japanese[2]	...	2·3-2·8	Bull

The following table shows the proportions of unsaponifiable matter found in some liver oils other than cod liver :—

Liver Oils.		Unsaponifiable.	Observer.
		Per cent.	
Shark liver oil .	Yellow, steamed	5·27	Fahrion
,,	Red	4·44	,,
,,	Yellow	1·24	,,
,,	Yellowish-red	0·93	,,
,,	Japanese	2·82	Allen
,,	Crude	8·70	,,
,,	Refined	0·70	,,
		10·25	,,
		17·30	,,
		10·34	,,
,,	Pale yellow, from *Scymnus borealis*	10·20	Lewkowitsch
,,	Japanese shark	14·4-21·5	Bull
Coal-fish liver oil	...	6·52	Mann
Tunny fish ,, ,,	...	1·0-1·8	Fahrion
Ling ,, ,,	...	2·23	Bull
Haddock ,, ,,	...	1·1	Lewkowitsch
Saith ,, ,, (coal-fish)	...	1·8	,,

Adulteration with mineral oils is readily ascertained by the determination of the saponification value and of the unsaponifiable matter, and by the examination of the latter. Vegetable oils are best detected by the phytosteryl acetate test, as the iodine value obviously does not furnish decisive results, although it may give the first indications,

[1] *Journ. Soc. Chem. Ind.* 1893, 607.

[2] Mann (*Journ. Soc. Chem. Ind.* 1903, 1357) records 7·18 per cent of unsaponifiable matter for an oil of the saponification value 186·7 (!).

if adulteration with oils having iodine values of less than 120 has taken place.[1] Confirmation of the presence of vegetable oils other than linseed oil[2] may also be obtained by the bromide test. In this connection it should be noted that cod liver oil substitutes are now being sold consisting of a mixture of genuine cod liver oil and iodised sesamé oil (Vol. III. Chap. XV. "Iodipin"). Such artificial cod liver oils will yield much less ether-insoluble bromide than a genuine oil does.

The detection of other liver oils in cod liver oil constitutes, in the present state of our knowledge, a very difficult problem. The determination of the unsaponifiable matter would appear to afford some guidance as to adulteration with other liver oils.

As a rule, other liver oils in commercial cod liver oil can be detected by the taste alone. Thus the ordinary pollock or coal-fish liver oil (saith oil, sej liver oil) has so unpleasant a taste that it cannot be admixed with cod liver oil without injuriously affecting the taste of the latter. But it should be noted that in the year 1903, when the prices of cod liver oil were exceptionally high, the liver oil of the pollock or coal-fish (saith oil) was actually prepared by the steam process, and such oil was largely added on the Continent to medicinal cod liver oils. It is within the author's experience that such steam extracted "saith oil" was offered even in this country as cod liver oil.

The bromide test also would lead to useful results, since the examination of shark liver oil in the author's laboratory has shown that the fatty acids yielded from 12·7 per cent to 15 per cent of ether-insoluble bromide only, as against 30 per cent in the case of genuine cod liver oil.

Of fish oils which may be used for the adulteration of cod liver oil the only oil that can be considered here, in the present state of the fish oil industry, is *salmon* oil, as all others, such as menhaden oil, herring oil, and sardine oils, are of too dark a colour and have too unpleasant a taste; but even salmon oil would betray its presence by a dark colour and inferior taste. Of the *blubber oils* only the best qualities of seal oil and whale oil could be used for adulteration. Their presence, if their quantities are not very large, would not be indicated without fail by the iodine absorption and the bromide tests. In case adulteration with seal oil or whale oil be suspected, and the chemical tests fail to furnish a decisive answer, the taste must be considered as one of the most important adjuncts in the detection of the adulterant or adulterants.

Since the detection of fish and blubber oils in cod liver oil is not always possible by means of the quantitative reactions, a number of

[1] A cod liver oil substitute is sold under the name of "*Fucol*"; it is prepared by digesting marine algæ with a vegetable oil (*Zeit. ang. Chem.* 1904, 397). English patent 2081, 1904.

[2] Töllner, United States patent 765,943.

colour tests have been recommended. I have examined the tests proposed by *Kremel*, *Meyer*, *Roessler*, and *Unger*,[1] but as I have found them useless, they are not described here. The colour test, however, described on p. 347, allows to differentiate fish and blubber oils from liver oils.

Notwithstanding the observations made by *Thomson* and *Dunlop*, and recorded above (p. 348), I would still recommend the sulphuric acid test as a reliable and rapid means of discriminating cod liver oil (and, indeed, all other fish liver oils) from fish oil (body oil) and blubber oils. It would, of course, not be permissible to judge by the depth of the blue-violet tint obtained with a sample of oil, as to whether adulteration with fish or blubber oil had taken place.

The **British Pharmacopœia** gives the sulphuric acid test as a reaction for the identity of cod liver oil. It has already been pointed out that the sulphuric acid test indicates only impurities which are due to lipochromes and colouring matters that have passed from the cellular tissue of the liver into the oil; and further, that with the improvement in the manufacturing processes the quantity of these by-products has decreased, so that during latter years the better-class oils showed the sulphuric acid colour reaction much more faintly than the liver oils prepared by the old processes. Indeed, the strongest colour reaction is given by shark liver oil, in the preparation of which little care is taken to prevent decay or putrefaction. A manufacturer should therefore endeavour to produce a cod liver oil which does not show the sulphuric acid test at all, or only very faintly.

The *British Pharmacopœia* prescribes the sulphuric acid test to be applied to the oil itself. The form in which this test is prescribed by the *German Pharmacopœia* is much preferable :—Dissolve one drop of oil in twenty drops of carbon bisulphide and add one drop of concentrated sulphuric acid, when a beautiful violet-blue colour appears at once, changing afterwards into red and brown. This test, however, cannot serve as an identity reaction, since other liver oils give the same *violet-blue* colour. Cod liver oils (as also other liver oils) which have become rancid do not show the violet-blue, but give at once the red colouration; oxidised cod liver oil gives a brown colour only. Thus an excellent cod liver oil which shortly after having been manufactured showed a bright violet-blue colouration in the sulphuric acid test, gave a dark brown colour in the same test a year later, although it had been kept protected from light and air.

The *United States Pharmacopœia* prescribes carbon tetrachloride in place of carbon bisulphide.

The detection of fish and blubber oils that have been fraudulently admixed in smaller or larger quantities with cod liver oil is, in the present state of our knowledge, still an unsolved problem. Seal and

[1] See second edition of this work, p. 486. Cp. also Wiebelitz, *Pharm. Zeit.*, 1903, 363. Unger's test actually indicated impurities due to decayed livers, which are at present carefully excluded.

whale oils yield much smaller proportions of ether-insoluble bromides than cod liver oil, as has been ascertained by *Walker* and *Warburton* in the author's laboratory. But Japanese fish oil and a deodorised fish oil have given numbers ranging from 23 per cent to 39 per cent of insoluble bromides, so that it is easy to prepare mixtures of cod liver oil, fish oil, and blubber oil yielding the average percentage of ether-insoluble bromides furnished by genuine cod liver oil. At present, exact chemical methods for the detection of these adulterants are still wanting. The organoleptic method must, therefore, be relied upon to guide in the examination of a suspected sample.

For the determination of the amount of **iodine** in cod liver oil or iodised cod liver oil, *Stanford*[1] proposed to saponify 300 grms. of oil with 40 grms. of caustic soda (free from iodine), then to evaporate to dryness and incinerate the soap in a porcelain crucible. The charred mass is next boiled out with water, filtered, and the filtrate evaporated to 300 c.c. 30 c.c. of this solution are then shaken with 12 c.c. of carbon bisulphide after a few drops of nitrosulphuric acid have been added (prepared by passing nitrous acid, evolved on heating starch or arsenious acid with nitric acid, into sulphuric acid). The amount of iodine dissolved in the carbon bisulphide is estimated colourimetrically by comparing the tint with that of another solution prepared similarly from a known amount of potassium iodide.

On shaking pure cod liver oil with water or alcohol no iodine passes into solution; fraudulently added potassium iodide can therefore thus be detected.

The best qualities of cod liver oil, as has been pointed out already, are used in pharmacy and for feeding calves. In order to mask the unpleasant taste which the older medicinal oils had—and which they are popularly believed to have still—various preparations are made from cod liver oil, such as effervescent cod liver oil or emulsified cod liver oils. (These, as also other substitutes for cod liver oil, such as iodised oils, phosphorised cod liver oil, and "fucol," will be described in Chap. XV.)

Lower qualities, *i.e.* the commercial cod oils, the coast cod oils, are used by tanners and curriers (see Chap. XVI. "Sod Oil").

In the examination of **commercial cod oil** for tanning and currying purposes, the amount of free fatty acids and unsaponifiable matter does not play the same important part as in the examination of medicinal oil.

As the livers which are worked up for cod oil are in a somewhat putrid condition, the amount of free fatty acids is considerable, and rises up to 25 per cent and more. The lower the amount of free fatty acids, the higher is the commercial value of the oil. The amounts of unsaponifiable matter occurring in brown cod oils may be gathered from the following table:—

[1] *Pharm. Journ.* (3) 14, 353.

Unsaponifiable Matter in Cod Liver Oils

Description of Oil.	Colour.	Unsaponifiable.	Observer.
		Per cent.	
Commercial oil, English . .	Yellowish-red	2·62	Fahrion
,, ,, ,,	Pale Yellow	0·6-1·68	Lewkowitsch
Brown cod oil[1] . . .	Brown	1·82	Fahrion
,, ,, . . .	,,	2·23	,,
,, ,, . . .	,,	2·68	,,
,, ,, . . .	,,	2·0-5·3	Lewkowitsch
,, ,, . . .	,,	1·87	Thomson and Ballantyne
,, ,, . . .	,,	7·3 (!)	Bull

Cod oil is frequently adulterated with fish oils, the detection and quantitative determination of which still offer a difficult problem, which has not been solved satisfactorily.

As cod liver oil, like fish oils, absorbs oxygen, the employment of it for paints and varnishes has been frequently suggested and also patented. Since the unsaturated fatty acids differ materially from those of linseed oil, no flexible skin can be obtained from cod liver oil. All these proposals are therefore valueless, although when prices of linseed oil are high, adulteration of "boiled oil" with liver (and fish and blubber) oils is frequently practised.

Procter and *Holmes*[2] have examined the oxygen absorption of cod liver oils and obtained the results stated in the following tables :—

Medicinal Cod Liver Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0[3]	0·924	1·4814	163·0
4	0·934	1·4819	163·0
8	0·937	1·4825	139·5
12	0·940	1·4831	131·5
16	0·952	1·4836	127·0
20	0·963	1·4847	122·0
24	0·969	1·4848	117·0

[1] Bull found 7·3-7·9 per cent of unsaponifiable matter in some brown oils. These figures suggest the presence of other liver oils.

[2] *Journ. Soc. Chem. Ind.* 1905, 1287.

[3] Original oil.

[TABLE

Cod Liver Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0 [1]	0·930	1·4812	156·0
3	0.930	1·4815	155·0
6	0·935	1·4820	152·0
9	0·937	1·4820	151·0
12	0·938	1·4825	150·0
15	0·940	1·4827	148·0
18	0·943	1·4828	145·0

Cod Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0 [1]	0·923	1·4810	154·0
3	0·928	1·4813	148·0
6	0·928	1·4815	148·0
9	0·928	1·4819	146·0
12	0·930	1·4819	144·0
15	0·930	1·4820	143·0
18	0·931	1·4822	143·0
21	0·932	1·4827	142·0
24	0·934	1·4828	141·0

Other liver oils are commercially of minor importance, and therefore need not be considered here individually. In the following table (see table facing p. 370) I collate the characteristics of some liver oils.

Shark liver oil appears to be no longer used in this country; at any rate it is not extracted here commercially. This oil is, however, prepared in considerable quantities in Iceland, and exported to the Continent for use in tanning; it is also manufactured at the coast of California, the coarser grades being employed in the making of tarpaulins and other oiled cloth. The livers from any shark caught by the trawlers are extracted, together with other livers, and therefore the "Coast cod oil" (p. 353) will contain varying quantities of shark liver oil.

Dog-fish liver oil is prepared from *Squalus acanthius*, L. This fish is caught on the coast of Oregon, Washington, and British Columbia in large quantities. One hundred livers are stated to yield from 6 to 8 gallons of oil. The oil is not generally kept separate from cod liver oil, and is sold in admixture with the latter for currying purposes.

The name "dog-fish" is also given to other species of fish closely allied to shark, such as *Scyllum laticeps*, *Acanthias vulgaris*, L. (spined dog-fish), *Lanina glauca* (tiger shark).

[1] Original oil.

In order to protect the fisheries the Federal Government of Canada offers a bounty for the capture of the dogfish, which on account of its voraciousness has become a serious menace to fisheries on the East Coast; hence considerable quantities of dogfish oil and dogfish "scrap" are obtainable in commerce.[1]

The changes which skate liver oil, coal-fish liver oil, and shark liver oil undergo on blowing with air at about 100° C. are set out in the following tables due to *Procter* and *Holmes*[2]:—

Skate Liver Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0[3]	0·926	1·4830	187·0
3	0·926	1·4830	185·0
6	0·926	1·4830	185·0
9	0·927	1·4831	174·0
12	0·929	1·4834	167·0
15	0·929	1·4835	163·0
18	0·930	1·4837	162·0
21	0·933	1·4840	160·0
24	0·937	1·4843	159·0

Shark Liver Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0[3]	0·910	1·4750	120·0
3	0·911	1·4752	119·0
6	0·911	1·4752	117·0
9	0·912	1·4754	111·0
12	0·913	1·4759	110·0
15	0·913	1·4760	108·0
18	0·913	1·4760	105·0
21	0·913	1·4760	104·0
24	0·916	1·4762	103·0

Coal-Fish Liver Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0[3]	0·921	1·4786	153·0
3	0·921	1·4787	151·0
6	0·921	1·4788	146·0
9	0·922	1·4788	141·0
12	0·923	1·4789	136·0
15	0·924	1·4790	135·0
21	0·927	1·4792	134·0
24	0·931	1·4794	130·0

[1] *Canada, Department of Agriculture Central Experimental Farm, Ottawa, Ontario,* 1906, p. 158; 1907.

[2] *Journ. Soc. Chem. Ind.* 1905, 1287. [3] Original oil.

Some characteristics of these liver oils and of other lesser known liver oils are given in the table opposite.

The livers of the crustacea (e.g. *Cancer pagurus*, *Palinurus vulgaris*) as also the livers of decapodes (*Birgus latro*) are very rich in oil. An examination of these oils has not been carried out hitherto.

Lesser known liver oils, see table opposite.

γ. Blubber Oils

In this group are comprised oils of different composition. Seal oil, whale oil, turtle oil, and dugong oil consist almost wholly of glycerides; dolphin oil, porpoise oil, and brown fish oil contain notable amounts of spermaceti, forming, as it were, intermediate members between true fatty oils and liquid waxes.

The last three members of this group—dolphin, porpoise, and brown fish oils—occupy an exceptional position on account of their containing considerable proportions of glycerides of volatile acids. In this respect turtle and dugong oils form intermediate links between these oils on the one hand, and seal and whale oils on the other.

SEAL OIL

French—*Huile de phoque.* German—*Robbentran, Seehundstran.*
Italian—*Olio di foca.*

For tables of characteristics see pp. 372-374.

Seal oil is obtained from the blubber of the various species of seal, such as *Phoca vitulina*, *Phoca grœnlandica*, *Phoca lagura*, *Phoca caspica*, etc.

The following seals occurring in the Antarctic Ocean have been described recently (National Antarctic Expedition, 1901-4, *Natural History*, vol. ii. Zoology, London, 1907): Weddell's seal (*Leptonychotes weddelli*), sea-leopard (*Stenorhynchus leptonyx*), crab-eating seal (*Lobodon carcinophagus*), Ross's seal (*Ommatophoca rossi*), sea elephant (*Macrorinus leoninus*), Hooker's sea lion (*Arctocephalus Hookeri*).

In the early times of "whaling," the oil was exclusively "tried" on board the whaling vessels, just as in the case of whale oil (see p. 376). Later, the seals were brought to rendering establishments on shore, and the blubber cut from the animal was thrown into large vessels of great height, in which the oil was pressed out from the lower layers by the superincumbent weight of the blubber, and the exuding oil was allowed to run off continuously. That running

R KNOWN LIVER OILS

ification alue.	Iodine Value.	Insolub Fatty Ac +Unsaponi	Specific Temperature Reaction.	Specific Rotatory Power.	Observer.
85·4	157·3	94·7	...	...	Lewkowitsch
87·9	191·1	...	322	$[\alpha]j = -0·20$	Thomson and Dunlop
...	155·9	95·79	...	...	Fahrion
88·8	154·2	93·3	...	...	Lewkowitsch
93·0	179	...	...	...	Liverseege[3]
87·2	186·4	...	300	...	Thomson and Dunlop
87·2	161·1	...	257	$[\alpha]j = -0·37$	Thomson and Dunlop
...	154·1	...	...	...	Lewkowitsch
84·1	132·6	...	...	...	Bull
88·0	133·0	...	...	...	Liverseege[5]
87·2	151·8	...	234	$[\alpha]j = -0·26$	Thomson and Dunlop
61·0	114·6	86·9	...	...	Lewkowitsch
1-148·5 4-163·5	111·9-114·9	...	...	...	Bull
57·2	128·3-136	...	...	...	,,
...	90	...	...	...	Eitner
...	...	...	...	...	Lewkowitsch
90·7	...	...	...	...	Lewkowitsch
...	154	...	...	...	Thomson and Dunlop
87·9	184·2	...	317	$[\alpha]j = -0·35$	,, ,,
69·7	126·4	...	...	$[\alpha]j = -1·67$	,, ,,
80·4 83·0	130·1 138·0	...	...	$-0·5°$ in 200 mm. tube	Mann Liverseege[7]

). [3] *Analy*ptical rotation $-0·5°$ in a 200-mm. tube.
soluble fatty acids, 52·3 at 40° C. le, p. 363.
action of fatty acids in butyro-refr

Face page 370, *Vol. II.*

out at first was pale, and almost free from smell. When, however, the blubber became rancid and even putrid, the oil obtained was rich in free fatty acids, and acquired, besides a dark colour, a nauseous taste. At present, seal oil is recovered by more rational methods, such as are described under the heading "Whale Oil," p. 377.

According as the oil is extracted from fresh blubber on board the steamer, or from blubber which has been brought to shore, the colour of seal oil varies.

The crude seal oils deposit "stearine" on standing, which is removed by filtering the oil. The "stearine" is sold as "fish stearine" or "fish tallow" for soap-making and currying purposes. The "stearine" from the first run oil is white and almost free from odour, whereas the "stearine" obtained from the last rendered oil is dark, high in its proportion of free fatty acids, and of bad odour. This "stearine" blackens easily on exposure to the atmosphere.

In commerce we find four brands of seal oil—water-white, straw, yellow, and brown seal oil; these represent the oils as they are obtained successively from the blubber by "rendering." The darkest quality is that which has been the longest in contact with the animal tissue, and has been extracted at the highest temperature.

The oil from *Phoca fœtida* (German—Ringelrobbe), occurring in the Baltic, notably differs from the seal oils furnished by the marine seals in respect of the iodine value. This must be attributed to the influence of food conditioned by the fauna of an inland sea.[1] Such influence becomes more pronounced still in the case of the seal oil from *Phoca fœtida*, var. *saimensis Nordkvist*, a variety of seal which has adapted itself for many generations to the fresh water of the Saima Lake.[2]

According to *Ljubarsky*[3] the mixed fatty acids from the *Caspian* oil consist roughly of 17 per cent of palmitic acid and 83 per cent of liquid acids. The latter yielded on oxidation a mixture of dihydroxypalmitic and dihydroxystearic acids, from which the presence of oleic acid and physetoleic acid (or hypogæic acid) in the original oil was inferred. *Ljubarsky* found no linolic acid, the presence of which had been recorded by *Kurbatoff*.[4]

Walker and *Warburton* obtained, however, in the bromide test 27·54-27·92 per cent of ether-insoluble brominated glycerides; the fatty acids yielded only 19·8-19·9 per cent of insoluble bromides, which behaved like the brominated products obtained from fish and liver oils.

Bull isolated from a specimen of Northern seal oil a liquid fatty acid absorbing 306·8 per cent of iodine.

In the elaïdin test seal oil gives a pasty mass, which separates from a liquid portion.

[1] Cp. Lewkowitsch, *Jahrbuch d. Chem.* xv. 420.

[2] This seems to me hardly tenable as a general proposition, inasmuch as carp fish oil has an iodine value of 84 only (cp. also my remarks in *Jahrbuch d. Chem.* xiii. p. 406; xiv. 440).

[3] *Journ. f. prakt. Chemie*, 1898, 26.

[4] *Berichte*, 25, Referate, p. 506.

Physical and Chemical Characteristics of Seal Oil

Source.	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
	°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
Phoca grœnlandica	15	0·925	Kremel	Deposits	Schaedler	189-196	Stoddart,	162·6	Thomson and
	,,	0·9249-0·9263	Chapman and Rolfe	"stearine" at 3		178-179	Deering Kremel	127-128	Dunlop Kremel
	15·5	0·9240-0·929	Allen	−2 to −3	Jean	189·3-192·8	Thomson and	142·2-152·4	Thomson and
	,,	0·9244-0·9261	Thomson and Ballantyne			190·7-196·2	Ballantyne Chapman and Rolfe	130·6	Ballantyne Lewkowitsch
	99	0·8733	Allen					129·5-141 [1]	Chapman and Rolfe
								147·1	Bull
								147·5	Lewkowitsch [2]
Phoca fœtida . .	15	0·9325	Schneider and Blumenfeld	...	...	188·2	Schneider and Blumenfeld	184·8	Schneider and Blumenfeld
Phoca fœtida *var.* saimensis Nordkvist	15	0·9321-0·9336	,,	...	...	1885·-189	,,	191·4-193·3	,,

[1] The bromine values of the specimens were 69·6 − 80, corresponding to iodine values 110·5-126·7.
[2] Water-white seal oil.

Physical and Chemical Characteristics of Seal Oil—continued

	Reichert Value.		Maumené Test.		Refractive Index.		
					Oleo-refractometer.		
	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At °C.	"Degrees.'	Observer.
Phoca grœnlandica	0·07-0·22	Chapman and Rolfe	92	Allen	22	+8	Jean
					22	+15	,,
			Specific Temperat. Reaction.		22	+30 to +36	Pearmain
					22	+32	Dowzard
			212-229	Thomson and Ballantyne	Butyro-refractometer.		
					25	72·7	Liverseege [1]
					40	64·0	,,
	Reichert-Meissl Value.				25	74·0	Lewkowitsch [2]
					40	65·0	,,
					25	76·2	Thomson and Dunlop
Phoca fœtida . .	1·12-1·69	Schneider and Blumenfeld	...	...	20	85·9	Schneider and Blumenfeld
Phoca fœtida *var.* saimensis Nordkvist	0·96-1·55	,,	...	...	35	75·3	,,
					20	87	,,
					35	78·4	,,

[1] *Analyst*, 1904, 210. The Valenta test of the sample was 88° C.

[2] Water-white seal oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.	
	Per cent.	Observer.	5° C.	Observer.	°C.	Observer.	°C.	Observer.
					Titer Test.			
Phoca grœnlandica	95·45 92·8-94·2	Kremel Chapman and Rolfe	...	...	15·5-15·9	Lewkowitsch	22-33	Chapman and Rolfe
Phoca fœtida	95·8	Schneider and Blumenfeld	0·9156	Schneider and Blumenfeld	17	Schneider and Blumenfeld	...	...
Phoca fœtida *var.* saimensis Nordkvist	95·6-95·85	,,	0·9172	,,	13-14	,,	14	Schneider and Blumenfeld

Physical and Chemical Characteristics of the Insoluble Fatty Acids—continued

Neutralisation Value.		Iodine Value.		Refractive Index. Butyro-refractometer.		
Mgrms. KOH.	Observer.	Per cent.	Observer.	At ° C.	"Degrees."	Observer.
190·4-196	Chapman and Rolfe	...	...	40	49·7	Liverseege
196·5	Schneider and Blumenfeld	186·5	Schneider and Blumenfeld	20 35	74 62·3	Schneider and Blumenfeld
196-198	,,	195·3-201·8	,,	20 35	74·1 64·3	,, ,,

The following table records the proportions of free fatty acids and unsaponifiable matter found by several observers :—

No.	Kind of Seal Oil.	Free Fatty Acids (as Oleic Acid).	Unsaponifiable Matter.	Observer.
		Per cent.	Per cent.	
1	Water-white .	0·2	...	Lewkowitsch
2	Pale . . .	0·9-1·5	...	„
3	Cold-drawn, pale	1·80	0·5	Thomson and Ballantyne [1]
4	Steamed, pale .	1·46	0·38	„
5	Tinged (brown) .	8·29	0·42	„
6	Norwegian . .	7·33	0·51	„
7	Northern . .	3·2	1·05	Bull
8	Very pale . .	0·98-1·13	...	Chapman and Rolfe [2]
9	Yellow . .	1·41	...	„
10	Light brown .	4·09	...	„
11	Dark brown .	19·95	...	„

It may be noted that *Thomson* and *Dunlop* obtained with an undoubtedly genuine and fresh seal oil a distinct violet colouration with sulphuric acid, similar to that given by liver oils. This specially prepared seal oil had the specific rotatory power $[\alpha]\,j = -0{\cdot}19$.

The best qualities of seal oil are used as burning oils in light-houses, or, when prices of cod liver oil are high, as an adulterant of cod liver oil; lower qualities of seal oil are used in soap-making and in the leather industries. The changes which seal oil undergoes in the sod oil manufacture is described in Chap. XVI.

The change suffered by seal oil on blowing with air at 100° C. is stated in the following table, due to *Procter* and *Holmes* [3] :—

Pale Seal Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value
Hours.			
0 [4]	0·932	1·4795	121·5
4	0·944	1·4798	121·5
8	0·955	1·4800	105·5
12	0·956	1·4808	100·0
16	0·961	1·4815	96·5
20	0·964	1·4820	94·5
24	0·968	1·4820	91·5

Seal oil is largely adulterated with mineral oils and rosin oils, the detection of which is, however, easy. A mixture of seal oil with various fish oils is frequently sold as seal oil. The detection of the adulterant is not easy, as neither the iodine value nor the

[1] *Journ. Soc. Chem. Ind.* 1891, 236. [2] *Ibid.* 1894, 843. [3] *Ibid.* 1905, 1287.
[4] Original oil.

bromide test furnish decisive indications. In the present state of our knowledge the taste and smell alone render some assistance in the examination.

WHALE OIL

French—*Huile de baleine.* German—*Walfischtran.*
Italian—*Olio di balena.*

For tables of characteristics see pp. 380, 381.

Whale oil is extracted from the blubber of various species of the genus *Balæna*, as *Balæna mysticetus*, Greenland or "Right" whale (northern whale oil); *Balæna australis* (southern whale oil);[1] *Balænoptera longimana*, *Balænoptera borealis* (Fin-back oil, Finner whale oil, Humpback oil: French—*Huile de rorqual*; German—*Finnfischtran*); *Rhachianectes glauca*, Cope (Japan). The northern whale oil is the "train oil" proper; but this name has become a generic name, and has been extended to all other "blubber oils" included in this group.

The blubber of whales caught in the northern seas of Europe was, in the early days of the whaling industry, "tried" on board the whalers, but in consequence of the low yield and also of the low quality of oil thus obtained, the whales are now brought into the "trying" stations situated in Finmarken, on the Lofotes, Farö, Shetland, and Hebrides Islands, and in Iceland.

To a large extent the American whalers still "try" the blubber on board ship and deliver the crude oil into the refineries of New Bedford, Mass., on the east coast, and of San Francisco on the west coast.

The whales caught in the whaling grounds adjacent to the South African coast, especially to that of Natal, will be brought into the "trying" station at Durban.

The "right whale" oil is of better quality than the "southern whale" oil. The "finner whale" oil is of still lower quality. Hence the finner whale was formerly neglected by the whalers, but at present even this kind of whale is eagerly pursued by them along the coasts of Norway and Newfoundland, as also to a smaller extent on the Asiatic coast of Russia, and the coast of Japan.

Besides the species of whales named, other kinds, such as the "orca" or "killer" whale, the "beluga" or white whale, are caught, especially by the American whalers, and the blubbers are rendered for whale oil.

The average yield of oil obtainable from the different species of whales is given in the following table:—

[1] The *Discovery* (National Antarctic Expedition, 1901-4), *Natural History*, vol. ii. Zoology, London, 1907), found no traces of the southern Right whale (*Balæna australis*) which Captain Ross had reported to be abundant in the 'forties of the last century, but met with the rorqual, the Australian whale (*Neobalæna marginata*), the "killer," and two new cetaceans.

[TABLE

Kind of Whale.	Yield in Barrels of 31·5 Gallons.
Right whale, Pacific	25 to 250
Right whale, Atlantic	25 ,, 150
Bowhead whale	30 ,, 250
Humpback whale, Pacific	10 ,, 110
Humpback whale, Atlantic	10 ,, 100
Finback whale, Pacific	10 ,, 70
Finback whale, Atlantic	20 ,, 60
Californian gray whale	15 ,, 60
Orca or killer whale	1 ,, 6
Beluga or white whale	1 ,, 3

The extraordinarily small quantity of cod fish caught off the coast of Norway in 1903, caused those interested in the cod-fishing industry to start an agitation, with the object of enforcing legislation against the killing of the whale off the coast of Norway, as the whales drive away the seals, who work the greatest destruction amongst the cod shoals. In consequence of this agitation a law was passed, which came into force on January 1, 1905, forbidding the killing of whales within Norwegian Sea territory and the landing of whales in the Norwegian rendering establishments.[1] This will, no doubt, increase the output of the rendering works in the Farö, the Shetlands, and the Hebrides Islands.[2]

According to the equipment of the blubber-rendering stations, the yield of the oil and also its quality vary. In the most modern works the blubber is stripped clean from flesh immediately after the arrival of the whaler, and care is taken to leave as little flesh as possible on the blubber. The latter is then cut into strips, which are thrown into chopping machines, whence the comminuted mass is immediately delivered into melting pans, and boiled with steam.[3] Five different qualities of whale oil are produced. The best quality is the oil which first runs off the blubber at the lowest temperature, known in commerce as "Whale Oil No. 0"; it is of a pale yellow

[1] It is doubtful whether this legislation will improve the yield of the fisheries, for it must be remembered that the movements of the cod and herring have always been erratic and are subject to unaccountable fluctuations, so that a period of good years has frequently been followed at every coast by a succession of lean years. This is further confirmed by the report of the British Vice-Consul at Bergen on the quantity of fat herring landed in the Tromso diocese :—

	1903.	1904.	1905.
	Hectolitres.	Hectolitres.	Hectolitres.
Nordland	261,274	61,853	8359
Tromso	90,530	..	600
Finmarken	21,072	2,765	..

[2] In consequence of the "Whale Fisheries (Scotland) Act" of 1907 the Fishery Board have prescribed a closed time for the prosecution of the whaling industry for a period of five weeks, extending from 1st June to 5th July (during the great summer herring fishery), within a distance of forty miles off the coasts of Shetland.

[3] A description of a modern installation for working up whale on land is given in *Oil, Paint, and Drug Reporter*, 1907, No. 10.

colour, and has but a faintly fishy smell. This oil contains a very small quantity of free fatty acids. The best brands are water-white, and are free from volatile fatty acids. On further boiling, the second quality ("Whale Oil No. 1") runs off; it is a little darker in colour, although still pale yellow. Its fishy smell is more pronounced than the oil of the first running.

These two qualities of oil are stored in large vessels, whereby they become clarified whilst depositing "stearine," which is filtered off, pressed in hydraulic presses, and sold as "whale tallow" for soap-making.

The residual mass in the boiling pans, together with the flesh of the whale, is cut up into strips or fairly large lumps, and is "tried down" in a digester under a pressure of 40-50 lbs. Thus the oil classed as "No. 2 oil" is obtained. This oil has a brown colour and a strongly developed fishy smell; its proportion of free fatty acids is considerably higher than in "Oil No. 1." In some stations "Whale Oil No. 2" is made from the blubber residues only, and does not contain any oil from the flesh. Hence it represents a superior article to the "No. 2 Oil" described in the preceding lines.

The bones are also worked up in the same manner, and yield a still inferior quality of oil. Such oil ("Whale Oil No. 3") is darker still, has a more strongly developed odour, and a high percentage of free fatty acids. "Whale Bone Oil" of commerce is, however, not exclusively made from the bones, except in those cases where the product is sold as "Bone Oil."

The oil obtained after the flesh has undergone some pronounced putrefaction ("Carcase Oil," "Whale Oil No. 4") is still darker, and more objectionable as regards smell and free fatty acids. In the three lowest qualities the proportion of unsaponifiable matter is somewhat considerable.

It must, of course, be understood that the different qualities described above, with the exception of "Whale Oil No. 0," vary within wide limits, so that no definite standards can be laid down. Specimens of Norwegian Whale Oils No. 1, No. 2, and No. 3, examined in my laboratory, gave the following acid values respectively:—3·97; 20·6; 53·42. If the oils have been filtered, they are sold as "Whale Oil, filtered." Even a "Filtered Whale Oil No. 4" occurs in commerce.

The residue remaining after the removal of the oil is worked up for manure, "whale guano" (cp. "Menhaden Oil").

This process is thoroughly carried out in Newfoundland (at Balena), where the Government has established several new plants. The carcases of the whale are there completely used up in the manufacture of oil, "stearine," bone meal or bones, and other articles of commerce.

If the whale is landed in a perfectly fresh state, cattle meal can be prepared from the fresh meat, as is being done in Iceland and in the Farö Islands. Some fresh meat is also consumed locally. The following table gives some statistics of the working up of whales in Iceland in the years 1900 and 1901:—

	1900.		1901.	
	Quantity.	Value.	Quantity.	Value.
Whale oil, barrels .	58,004	£101,089	64,919	£101,451
Whale bone, cwts. .	7,622	20,385	1,356	2,752
Cattle meal . .	9,122	3,028	5,711	1,745
Bone meal . . .	9,518	1,402	8,750	1,357
Guano . . .	8,502	1,767	5,684	937
Bones . . .	8,600	694	2,000	167

Later statistics up to 1904 are not complete and are therefore not given here. Since taxes are being imposed on each whale landed in Iceland, the Farö, and the Shetland Islands, etc., more complete statistics may be expected in future.

The Shetland whaling industry is, in consequence of the above-mentioned Norwegian law, on the increase. The number of whales caught during the season 1904 amounted to 412.

In 1905, 2364 whales were killed near Spitzbergen, Iceland, the Farö, Shetland, and Hebrides Islands. 72,420 barrels of whale oil are stated (!) to have been produced.

The total production of whale oil amounts at present to 3,000,000 gallons per annum ; of these 900,000 are produced by the Norway fisheries, 750,000 by the United States fisheries, and the remainder by Scotland, Russia, Newfoundland, Japan, and other countries.

The following table gives some characteristics of various brands of whale oil. The numbers are due to *Bull* :—

	Specific Gravity at 15° C.	Acid Value.	Saponific. Value.	Iodine Value.	Unsaponifiable.
Antarctic right whale oil (America)	0·9257	0·56	183·1	136·0	1·46
Whale oil No. 1, unrefined (Finmarken)	0·9181	0·86	188·6	104·0	2·36
Refined (Glasgow) . .	0·9214	1·4	184·7	113·2	2·33
Arctic whale oil, refined (America)	0·9234	1·9	185·0	117·4	2·11
Crude white whale oil (America)	0·9222	2·5	183·9	127·4	1·37
Whale oil No. 2, unrefined (Finmarken)	0·9182	3·6	188·3	...	3·3
Yellow whale oil, refined (Glasgow)	0·9232	10·6	185·9	110·0	1·89
Whale oil No. 3, refined (Finmarken)	0·9162	26·5	185·7	96·0	2·42
Brown whale oil, refined (Glasgow)	0·9272	37·2	160·0	125·3	3·22
Whale oil No. 4, unrefined (Finmarken)	0·9205	58·1	182·1	89·0	3·4
Dark whale oil, refined (Glasgow)	0·9170	98·5	178·3	103·1	3·03

Physical and Chemical Characteristics of Whale Oil

Oil from	Specific Gravity.			Saponification Value.		Iodine Value.		Reichert Value.		Maumené Test.		Refractive Index.					
												At 20° C.	Observer.				
	°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	1·4762	Tsujimoto				
												Oleo-refractometer.					
Balæna and Balænoptera species	15	0·9170-0·9272	Bull	193·1 [1]	Deering	110·1	Thomson and Ballantyne	0·7-2·04	Lewkowitsch	91 [3]	Allen	"Degrees." At 22° C.	Observer.				
				188·5	Stoddard					85-86 [1]	Dobb						
	15·5	0·9307	Allen	188·8	Thomson and Ballantyne					92 [1]	Archbutt						
		0·9221-0·9225	Schweitzer and Lungwitz			121·3-127·7	Schweitzer and Lungwitz			61	Jean						
	15	0·9193	Thomson and Ballantyne	188·5	Lewkowitsch	136·0 [2]	Bull					+30·5 +42 to +48	Jean Pearmain				
				187·9-194·2	Schweitzer and Lungwitz	117·7	Lewkowitsch [4]					Butyro-refractometer.					
	98·99	0·8725	Allen							Specific Temperature Reaction.		At °C.	"Degrees."	Observer.			
										157	Thomson and Ballantyne	25	65	Liverseege [5]			
												40	56	,,			
												25	68 [4]	Lewkowitsch			
												40	59 [4]	,,			
Rhachianectes glauca, Cope	15·5	0·9254	Tsujimoto	192·6	Tsujimoto	146·6	Tsujimoto					25	68 [6]	,,			
												40	59 [6]	,,			

[1] Southern whale oil. [2] Antarctic right whale. [3] Northern whale oil. [4] Whale oil, No. 1, filtered.
[5] *Analyst*, 1904, 211. Optical rotation of the sample, −0·5° in a 200-mm. tube. Valenta test 100° C. [6] Whale oil, No. 0.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Iodine Value.		Butyro-refractometer.			Ether-insoluble Bromides.	
Per cent.	Observer.	At 100° C. (Water 100° C. = 1.)	Observer.	°C.	Observer.	° C.	Observer.	Per cent.	Observer.	At °C.	"Degrees."	Observer.	Per cent.	Observer.
				Titer Test.										
93·5	Lewkowitsch	0·8922	Archbutt			27	Jean	130·3-132	Schweitzer and Lungwitz	40	43·3	Liverseege	27·77[1]	Lewkowitsch
				22·9-23·9	Lewkowitsch	14-15 16 16·2 18	Schweitzer and Lungwitz						27·81[2]	Tsujimoto
								Liquid Fatty Acids.						
								144·7	Clapham [3]					

[1] Filtered whale oil of best quality.

[2] Oil from *Rhachianectes glauca*, Cope.

[3] Determined in the author's laboratory.

The chemical composition of the whale oil fatty acids has not yet been established satisfactorily. The deposited "stearine" consists to a large extent of palmitin. The iodine value of a sample of pressed cake examined in the author's laboratory was 37·9. Volatile fatty acids are absent; the high *Reichert* values recorded by earlier observers are undoubtedly due to the specimens examined having been highly rancid.

Hehner and *Mitchell* obtained from a specimen of whale oil 25 per cent of a brominated glyceride, to which they ascribed the composition $C_3H_5(C_{18}H_{30}O_2Br_6)_2(C_{18}H_{33}O_2Br_2)$. A specimen of whale oil examined in my laboratory by *Walker* and *Warburton* gave only about 16 per cent of a highly brominated glyceride, whilst the fatty acids yielded 12·4 per cent of an ether-insoluble brominated acid, which behaved like the products derived from other marine animal oils, in that it blackened at 200° C., without melting. This specimen of whale oil was a somewhat old one which evidently had undergone some oxidation, for more recently a number of whale oils examined in my laboratory gave from 20·09 per cent to 22·59 per cent of ether-insoluble brominated acids. Recently *Tsujimoto* found in a freshly prepared whale oil (from *Rhachianectes glauca*) 27·81 per cent of ether-insoluble brominated fatty acids. The fatty acid from which the ether-insoluble bromides were derived has been identified by *Tsujimoto* as clupanodonic acid. The 27·81 per cent of ether-insoluble brominated fatty acids would correspond to 8·39 per cent of clupanodonic acid. This is in excellent agreement with the amount of insoluble bromides found recently by the author for a freshly filtered whale oil of best quality, namely, 27·77 per cent.

Bull isolated from a number of whale oils some highly unsaturated fatty acids, having iodine values ranging from 251 to 315·6. The readiness with which low-class whale oils become oxidised on exposure to the air may explain the fact that *Fahrion* found from 0·39 to 1·44 per cent of oxidised fatty acids in some specimens.

The amount of unsaponifiable matter also varies with the quality of the oil. The following table contains the amounts of unsaponifiable matter determined in commercial oils. The lower the quality of the oil, the larger the amount of unsaponifiable matter (and the lower, consequently, the saponification value).

Unsaponifiable Matter in Whale Oils

Description of Oil.	Per cent.	Observer.
Norwegian, yellowish-red	0·65	Fahrion
,, yellowish-brown	1·26	,,
,, brown	1·37	,,
Pale	1·22	Thomson and Ballantyne
,, refined	0·92-3·72	Lewkowitsch
Samples described in table, p. 379.	1·4-3·4	Bull

The iodine value of a given specimen of whale oil depends on the amount of "stearine" left in the oil; hence the great variations in the numbers recorded in the tables are readily explained.

Whale oil is largely adulterated with rosin oil, the detection of which is simple. More difficult is the detection of admixed seal oil, on account of the great similarity of the two oils; at present this is practically impossible by chemical means—taste alone permits the recognition of seal oil.

The "water-white" and "pale" brands of whale oil are used as burning oil and in soap-making. The lower qualities are employed for leather-dressing.

Whale oil is also largely used in jute batching, for tempering steel, and as a lubricant for screw cutting machines.

The changes which whale oil undergoes in the preparation of sod oil will be described in Chap. XVI. The change which takes place in whale oil on blowing with air at 100° C. may be gathered from the following tables, due to *Procter* and *Holmes*[1]:—

Whale Oil

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0	0·933	1·4762	121·0
4	0·936	1·4765	112·0
8	0·937	1·4766	97·5
12	0·948	1·4767	89·0
16	0·949	1·4770	87·0
20	0·950	1·4773	87·0
24	0·950	1·4773	86·0

[1] *Journ. Soc. Chem. Ind.* 1905, 1287.

[TABLE

Whale Oil, Filtered.[1]

Blown.	No. 1.		No. 2.		No. 3.	
	Refractive Index.	Dispersion.	Refractive Index.	Dispersion.	Refractive Index.	Dispersion.
Hours.						
0	1·4740	40·0	1·4740	39·9	1·4732	39·9
3	1·4751	40·1	1·4744	40·0	1·4740	40·0
4	1·4752	40·2	1·4745	40·3	1·4740	40·0
5	1·4753	40·2	1·4747	40·3	1·4750	40·2
6	1·4758	40·3	1·4748	40·4	1·4755	40·3
7	1·4760	40·4	1·4750	40·5	1·4757	40·5
8	1·4762	40·5	1·4754	40·5	1·4759	40·6
9	1·4763	40·5	1·4756	40·5	1·4761	40·6
10	1·4765	40·5	1·4756	40·5	1·4763	40·6
11	1·4768	40·7	1·4757	40·6	1·4768	40·6
12	1·4770	40·7	1·4758	40·6	1·4770	40·7
13	1·4770	40·7	1·4760	40·6	1·4770	40·7
14	1·4771	40·7	1·4760	40·6	1·4771	40·7
15	1·4773	40·7	1·4761	40·7	1·4773	40·7
16	1·4773	40·7	1·4761	40·7	1·4773	40·7
17	1·4773	40·8	1·4762	40·7	1·4773	40·7
18	1·4774	40·8	1·4763	40·7	1·4774	40·7
19	1·4779	40·8	1·4765	40·8	1·4776	40·8
20	1·4780	40·8	1·4765	40·8	1·4776	40·8
21	1·4780	40·8	1·4765	40·8	1·4776	40·8
22	1·4752 (?)	40·8	1·4765	40·8	1·4777	40·8
23	1·4782	40·8	1·4765	40·8	1·4777	40·8
24	1·4782	40·8	1·4765	40·8	1·4777	40·8

TURTLE OIL

French—*Huile de tortue.* *German—Schildkrötenöl.*
Italian—*Olio di tartaruga.*

For tables of characteristics see p. 385.

This oil, the characteristics of which are described by *Zdarek* in the following tables, is the body-fat from *Thalassochelys corticata*, Rond. The oil has a yellow colour.

The specimen described by *Sage* appears to have been obtained, according to private information given to the author (by Mr. Ulcoq, Chairman of the Delegates of the Colony of Mauritius at the Franco-British Exhibition, 1908), from turtle belonging to the family *Testudo* (Chersidæ). The specimen of oil shown at the Exhibition was of a pale yellow colour, and had a slightly fishy taste.

The specimens examined had the acid value 0·57 (*Zdarek*) and 1·1 (*Sage*).

This oil is now being prepared commercially in Mauritius.

[1] The samples used for these experiments were supplied by the present author from bulk lots prepared on a large scale.

Physical and Chemical Characteristics of Turtle Oil

Specific Gravity.		Solidifying Point. °C.	Melting Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.		Observer.
°C.							°C.		
42·5	0·9198	10·0	23-27	209	112	4·6	30	1·4677	Zdarek [1]
25	0·9192	19-18	24-25	211·3	111·0	4·8	50	1·4665	Sage [2]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value.	Observer.
28·2	30·2	268	119	Zdarek

[1] *Zeit. f. physiolog. Chem.* 1903, 460.

[2] *Chemist and Druggist*, 1906, 691.

DUGONG OIL, MANATEE OIL

French—*Huile du dugong, Huile de lamantin.* German—*Dugongöl.*
Italian—*Olio di vacca marina.*

This oil is obtained from the blubber of the sea-cow (*Halicore australis* and *Halicore indicus*), a herbivorous mammal living near the shores of the Indian Archipelago, in the Persian Gulf, and in the Red Sea. In the Indian Ocean the dugong is met with in large herds, the animals reaching there a length of 5·5 to 6 metres, whereas the dugong occurring near Australia only reaches a length of 3·6 to 4·25 metres.

Physical and Chemical Characteristics of Dugong Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert Value.	Refractive Index.	
				Butyro-refractometer.	
At 60° F.	Mgrms. KOH.	Per cent.	cc. $\frac{1}{10}$ norm. KOH.	"Degrees."	Observer.
0·9203	197·5	66·6	2·5	60·3 at 25° C.	Mann [1]
				52·0 at 40° C.	Liverseege [2]

The specimen of dugong oil examined by *Mann* [1] is stated to contain 3·74 per cent of unsaponifiable matter, and 2·39 per cent of free fatty acids; that examined by *Liverseege* [2] had the acid value 5 and yielded 0·9 per cent of unsaponifiable matter. Its optical rotation is stated to be − 0·1° in a 200-mm. tube. The refraction of the insoluble fatty acids in the butyro-refractometer at 40° C. was 37·7 "degrees."

The dugong oil from the Indian species serves the same purposes as cod oil and whale oil. The oil from the Australian species is used as a burning oil.

DOLPHIN OIL, BLACKFISH OIL

French—*Huile de dauphin.* German—*Delphintran.*
Italian—*Olio di delfino.*

For table of characteristics see p. 387.

Dolphin oil, from the blubber of the blackfish (bottlenose dolphin), *Delphinus globiceps*, Lam., forms an intermediate link between whale oil (consisting nearly wholly of glycerides) and sperm oil (a true wax).

[1] *Journ. Soc. Chem. Ind.* 1903, 1357. [2] *Analyst*, 1904, 211.

Physical and Chemical Characteristics of Dolphin Oil

	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index.		
	At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At ° C.		Observer.
Body oil	15	0·9266	Bull	Deposits spermaceti from 5 to −3	Chevreul	197·3	Moore	99·5	Moore	5·6	Moore	15	1·4708	Utz
						203·4	Bull	126·9	Bull			20	1·4682	,,
Jaw oil						290	Moore	32·8	Moore	65·92	Moore	Butyro-refractometer.		
												At ° C.	"Degrees."	Observer.
												15	67·7	Utz
												20	63·6	,,

The oil obtained from the blubber is kept separate from that obtained from the cavities in the head and from the jaw of the blackfish. We therefore differentiate between *dolphin body oil* and *dolphin jaw oil.*

Body Oil.—The yield of oil from the *blubber* of a dolphin averages from one-sixth to four barrels of 31·5 gallons capacity.

This oil is of a pale yellow colour. On standing it deposits spermaceti (cetyl palmitate) [*Chevreul*]. *Bull* [1] found amongst the liquid fatty acids 14·3 per cent of an acid having the iodine value 285·5, and the neutralisation value 313·2. The oil is remarkable on account of the notable amount of glycerides of volatile fatty acids it contains, a characteristic which it shares with porpoise oil. Hence the amount of insoluble fatty acids + unsaponifiable is only 93·07 per cent (*Moore*).

Bull isolated from a specimen of body oil 2·01 per cent of unsaponifiable matter.

Jaw Oil ("Melon oil" [2]).—The proportion of glycerides of volatile acids in the jaw oil, *i.e.* the oil from the soft blubber contained in the head and jaw of the blackfish, is larger than in the body oil.

The jaw oil (as also porpoise jaw oil and brown fish oil) is distinguished from all other vegetable and animal oils by the extraordinarily high amount of volatile acids it contains. Hence the proportion of insoluble fatty acids (+ unsaponifiable matter) is only 66·28 per cent (*Moore*).

The jaw oil has a straw-yellow colour and a not unpleasant smell. It is used for lubricating fine machinery, such as watches and typewriting machines.

PORPOISE OIL

French—*Huile de marsouin.* German—*Meerschweintran, Schweinfischtran.* Italian—*Olio di porco marino.*

For table of characteristics see p. 389.

Porpoise oil is obtained from the brown porpoise, *Delphinus phocæna*, L. In the case of porpoise oil also, we differentiate between *body oil* and *jaw oil.*

Body Oil.—The *body* oil was examined first by *Chevreul*, who discovered in it "valeric" acid, named by him "acide phocénique." On account of its somewhat high proportion of unsaponifiable matter, this oil appears to form an intermediate link between the blubber oils and the liquid waxes.

[1] *Chem. Zeit.* 1899, 1044.

[2] Cp. Archbutt and Deeley, *Lubrication and Lubricants*, p. 115.

Physical and Chemical Characteristics of Porpoise Oil

	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Maumené Test.		Refractive Index. Butyro-refractometer.		
	°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	°C.	"Degrees."	Observer.
Body oil	15	0·9258	Bull	−16	Chevreul	216-218·8	Allen	119·4	Bull	11-12	Allen	50	Allen	25	54·8	Thomson and Dunlop
	15	0·926	Thomson and Dunlop			195	Bull	88·3	Thomson	23·45[1]	Steenbuch[2]			40	46·3	
	16	0·937	Chevreul			256·6	Thomson and Dunlop		and Dunlop	40·7[1]	Thomson and Dunlop					
	99 (water 15·5=1)	0·8714	Allen													
Jaw oil, skimmed and strained	15	0·9258	Bull			253·7	Moore[3]	49·6	Moore[3]	47·77	Moore[3]					
						272·3	,,	30·9	,,	56·00	,,					
						269·3	Bull	21·5	Bull	65·8[1]	Steenbuch					
Jaw oil, not skimmed nor strained						143·9	Moore	76·8	Moore	2·08	Moore					

Insoluble fatty acids + unsaponifiable, 91·04 per cent. Neutralisation value of insoluble fatty acids, 203 (Hart[4]).

[1] Reichert-Meissl values 46·9 and 131·6 and Reichert-Wollny value 81·4, halved for the sake of comparison.

[2] *Zeit. angew. Chem.* 1899, 64.

[3] *Journ. Soc. Chem. Ind.* 1890, 331.

[4] *Chem. Zeit.* 1908, 819. The spec. grav. of the oil (evidently body oil) was 0·9302 at 15° C., saponific. val. 222·2, and Maumené test 61° C.

The amount of volatile fatty acids is somewhat high. No further extended inquiry has been made into the composition of the oil (especially into that of the volatile fatty acids) since *Chevreul's* investigation. As the oil can now be obtained somewhat easily in commerce a renewed examination is desirable. No doubt the amount of insoluble fatty acids will be found comparatively low. The body oil is pale yellow and resembles the dolphin body oil. It is stated to consist of the glycerides of "valeric," palmitic, stearic, and oleic (and physetoleic ?) acids.

Thomson and *Dunlop* found a specimen of porpoise body oil to be dextro-rotatory, $[\alpha]j = +0{\cdot}76°$ (whereas all the liver oils are lævo-rotatory). This specimen gave a violet colour in the sulphuric acid test described above (p. 347) as a characteristic test for liver oils. It is important to note this, as on the strength of this colour test alone such porpoise oil might be declared as adulterated with liver oil. A specimen of body oil examined by *Bull* contained 3·7 per cent of unsaponifiable matter. *Bull* isolated from a body oil 19·48 per cent of fatty acids having the iodine value 322·5 and the neutralisation value 191·4.

Jaw Oil.—The *jaw* oil simulates the corresponding dolphin oil in its composition.

The jaw oil is easily soluble in alcohol at 70° C.; it is therefore possible to extract it from a mixture of the body and jaw oils. The amount of insoluble fatty acids varies from 61·41 and 72·05 per cent in skimmed and strained jaw oil, to 96·5 per cent in unskimmed and unstrained jaw oil (*Moore*).

In a specimen of porpoise jaw oil *Bull* found 16·4 per cent of unsaponifiable matter, and 21·13 per cent of fatty acids having the iodine value 31·3 and the neutralisation value 367·8. This points to large proportions of "(iso)valeric" acid.

The oil is used, like dolphin oil, for lubricating purposes.

BROWN FISH OIL

French—*Huile de marsouin brun.* German—*Braunfischöl.*
Italian—*Olio di pesce porco.*

For tables of characteristics see p. 391.

This oil is obtained from the brown fish, *Phocæna communis*, belonging to the *Delphinidæ*. The characteristics given in the table refer to the *body* oil. The oil has a pale yellow colour, and possesses a not unpleasant smell. Like porpoise oil it is distinguished by a high proportion of volatile fatty acids. Hence it yields only 85·5 per cent of insoluble fatty acids + unsaponifiable. The acid value of the specimen examined was 1·2.[1]

[1] Schneider and Blumenfeld, *Chem. Zeit.* 1906, 53.

Physical and Chemical Characteristics of Brown Fish Oil

Specific Gravity at 15° C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value.	Refractive Index. Butyro-refracto-meter.	
				°C.	"Degrees.'
0·9334	224·8	111·2	42·1	25	62·7

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable. Per cent.	Specific Gravity at 15° C.	Solidifying Point. °C.	Neutralisation Value. Mgrms. KOH.	Iodine Value. Per cent.	Acetyl Value. Mgrms. KOH
85·5	0·9121	18	207	126	4·55

The oils from marine animals described above were somewhat closely examined, on account of the commercial importance they possess. The chemistry of fish oils from fresh-water fish—with the exception of carp oil (p. 347)—has not yet been investigated; no doubt because these oils have only scientific interest. In view of the fact that the iodine value of carp oil is much lower than that of the marine fish oils, it would appear interesting to examine a larger number of oils prepared from fresh-water fish. The fresh-water eel, containing about 30 per cent of oil (calculated to dry substance), would seem to be a suitable subject for investigation. Possibly a difference might be established between oils from marine fish and oils from fresh-water fish with respect to their iodine value, although the differences in the seal oils from *Phoca vitulina* and *Phoca fœtida* var. *saimensis* (cp. p. 371) do not seem to favour the conjecture that the oils from sweet-water fish may be found to exhibit lower iodine values than the marine animal oils.

(2) Terrestrial Animal Oils

Hitherto only four oils, viz. sheep's foot, horse's foot, neat's foot oil, and egg oil, had been described under this head, and no differentiation was made on account of their origin from quadrupeds and birds respectively, as egg oil seems to resemble the first-named three oils in many respects, such as low iodine value and elaïdin test.

Oils from other classes of terrestrial animals did not offer sufficient practical interest to induce an examination. Recently, however, the chrysalids, which form a by-product of the silk industry, have been treated on a commercial scale to recover the not inconsiderable amount of oil contained in them. The examination of this oil, carried out by the author, showed that, judged by the iodine value alone, it would have to be classed amongst semi-drying oils. A further support is found in that this oil yields a soft buttery elaïdin.

Although it may be somewhat premature to subdivide the terrestrial animal oils according to their origin into (1) oils from insects, (2) oils from birds, (3) oils from quadrupeds, this order may be suitably adopted in the following enumeration of these oils.

CHRYSALIS OIL [1]

French—*Huile de chrysalide.* German—*Chrysalidenöl.*
Italian—*Olio di crisalide.*

This oil is obtained by extracting the chrysalids (pupæ) of silkworms (*Bombyx mori*) by means of solvents. A sample extracted in the author's laboratory with ether from a batch of chrysalids (which had also been extracted on a manufacturing scale) yielded 27·2 per cent. of a clear, dark yellow oil, from which considerable quantities of crystalline warts separated. The oil had the following characteristics :—

Saponification value	194·0
Iodine value	117·8 [2]
Unsaponifiable	4·86 per cent.
Acid value	62·8

The crude oil prepared on a large scale from the same chrysalids had a dark brown colour, and a distinct smell resembling that of fish oil. By filtering over Florida earth the oil became much clearer. On standing, solid particles separated as amorphous flocks, no doubt

[1] Lewkowitsch, *Zeit. f. Untersuch. d. Nahrungs- und Genussm.* 1906, xii. 659 ; 1907, xiii. 552

[2] See Appendix.

due to traces of solvent still adhering to the commercial oil. The commercial oil had the following characteristics :—

Specific gravity at 40° C. (water at 40° = 1)	0·9105
Solidifying point	10°-7° C.
Saponification value	190·0
Iodine value	116·3
Unsaponifiable	2·61 per cent.
Acid value	27·51
Mean molecular weight of the insoluble fatty acids	281·7
Solidifying point of the insoluble fatty acids	34·5° C.

The considerably lower acid value of the commercial oil is due to the oil in the chrysalids extracted by the author having undergone somewhat pronounced hydrolysis (see Vol. I. Chap. I.).

In the elaïdin test the oil yields a soft buttery mass.

This oil being the first obtained from insects,[1] it became important to ascertain whether the unsaponifiable matter contained cholesterol like all the oils and fats of animal origin.

A considerable quantity of the unsaponifiable matter was treated with acetic anhydride, whereby 84·67 per cent of the unsaponifiable matter (corresponding to 2·21 per cent of the chrysalis oil) was dissolved, whereas 15·33 per cent (corresponding to 0·40 per cent of the chrysalis oil) remained undissolved. This last substance melted between 54° and 62° C., and is undoubtedly a hydrocarbon.

The substance dissolved in acetic anhydride was recrystallised five times, and finally yielded in the fifth crystallisation crystals of the melting point 114° C.

The details are the following :—

Melting point of the 2nd crystallisation	107·5-113° C.
,, ,, ,, 3rd ,,	110-113° C.
,, ,, ,, 4th ,,	112-113·5° C.
,, ,, ,, 5th ,,	114° C.

Hence the unsaponifiable matter contains cholesterol.

Menozzi and *Moreschi*,[2] who found "about 10 per cent" of unsaponifiable matter, isolated from this by extraction with 70 per cent alcohol a higher alcohol, melting after repeated crystallisation at 148° C., which they consider differs from the ordinary cholesterol (Vol. I. Chap. III.) and has been named "*bombicesterol*." The acetate of this alcohol melted in the impure state at 112-114° C.; after *one* crystallisation the melting point rose to above 120° C., and after repeated crystallisations to 129° C. On applying *Windaus'* method[3] a small quantity of an acetate melting at 114° C. was obtained, and a larger quantity of an acetate melting at 129° C. On passing a pure acetate of the melting point 129° C. through *Windaus'* process, an acetate melting at 129° C. was obtained.

[1] It may, however, be mentioned that *R. Dubois* stated (*Oil, Paint, and Drug Reporter*, 1903, 24) that he had prepared oil from the eggs of locusts.

[2] *Rendiconti della R. Accad. dei Lincei*, 1908, i. p. 95.

[3] *Berichte d. d. Chem. Ges.* 1906, 518. Cp. Lewkowitsch, *Jahrbuch der Chemie*, xvi. 406.

Menozzi and *Moreschi* further isolated from the unsaponifiable matter two hydrocarbons, one melting at 62·5° C., and having the composition $C_{28}H_{58}$, and a second one, which also appears to belong to the saturated series, melting at 41°-42° C.

Tsujimoto[1] states that chrysalis oil is being prepared in Japan by steaming the powdered dry chrysalids and expressing the mass in a screw or wedge press. A specimen of *pupæ* was found to contain—

Oil	26·6 per cent.
Ash	3·77 ,,
Water	5·48 ,,

By extracting with petroleum ether boiling below 80° C., an oil was obtained having the following characteristics :—

Oil—

Specific gravity at 15·5° C.	0·9280
Saponification value	194·12
Iodine value	131·96[2]
Reichert-Meissl value	3·38
Unsaponifiable matter	1·63
True acetyl value (Lewkowitsch)	19·72
Refractive index at 20° C.	1·4757

Fatty Acids—

Insoluble fatty acids + unsaponifiable	94·5 per cent.
Specific gravity 100° C. (water at 15·5 = 1)	0·8513
Melting point	36·5° C.
Solidifying point	77-78° C.
Neutralisation value	199·34
Mean molecular weight	281·43
Iodine value	135·83[2]

The oil had the acid value 18·68. The fatty acids were resolved by the lead-salt-ether method into 75 per cent unsaturated fatty acids (of the iodine value 178·73) and 25 per cent (by difference) of saturated fatty acids (of the melting point 57° C.). Amongst the saturated fatty acids palmitic acid was identified ; stearic acid is probably not present.

The unsaturated fatty acids consist of oleic, linolenic, and isolinolenic acids. The amount of ether-insoluble bromides—melting at 178° C.—was 11·94 per cent, corresponding to 4·38 per cent of linolenic acid (including isolinolenic acid).

The unsaponifiable matter after recrystallisation from 90 per cent alcohol yielded crystals, melting at 138·5° C. ; after repeated purification they melted at 143·5° C. Their crystalline form is stated to

[1] *Journ. Coll. Engineering, Tokyo*, 1908, vol. iv. No. 3. This author refers in a footnote to three papers published in 1905 (*in Japanese*) : "Chrysalis Oil Manufacture in the Nagano and Gunma Prefectures," *Report of Industr. Exper. Station*, Tokyo, vol. ii. 1905, 473 ; "On Chrysalis Oil," by K. Zasshi ; and "On the Fatty Acids of Chrysalis Oil," by K. Zasshi.

[2] See Appendix.

closely resemble that of phytosterol. The acetate obtained from this alcohol by *Bömer's* method melted at 125·5° C. From a second sample of chrysalis oil *Tsujimoto* obtained an alcohol, melting at 137-139° C., the acetate of which melts at 125° C. *Tsujimoto* concludes therefrom that the alcohol in chrysalis oil is phytosterol.

Evidently a fresh examination is required in order to settle the question as to whether this oil contains cholesterol or phytosterol, or bombicesterol, or two different alcohols.

The melting points found by *Lewkowitsch* in five crystallisations (see above) would seem to exclude the possibility of a small amount of hydrocarbon having been persistently retained by the acetate (cp. tables "Melting Points of Cholesteryl Acetate with Paraffin Wax" under "Lard"). The fact that *Menozzi* and *Moreschi*, after separating off the hydrocarbons carefully and applying *Windau's* method of separation, did obtain an acetate melting at 114° C. in addition to bombicesterol, would seem to prove that what *Tsujimoto* regarded as "phytosterol" was, in truth, a mixture of cholesterol and bombicesterol. However, an explanation is still required for the fact that *Lewkowitsch* obtained cholesterol only.

Since this oil can be obtained without difficulty, it is destined to find an outlet in the soap industry in considerable quantities.

EGG OIL

French—*Huile de jaune d'œuf.* German—*Eieröl.*
Italian—*Olio di uovo.*

For tables of characteristics see p. 396.

Egg oil is prepared commercially from the yolk of hard-boiled hen's eggs either by pressure or by solvents. Another process consists in separating the yolk of fresh eggs from the white, and heating the yolk until the bulk of the water has evaporated off. The dried mass is then placed in bags and expressed between hot plates. The expressed oil is then filtered. *Paladino* and *Toso* [1] obtained, by expressing boiled eggs, 25 to 35 per cent of oil; *Kitt*,[2] by using ether as a solvent, 19 per cent only. The ethereal extracts contain, besides egg oil, other substances, notably lecithin.

The expressed oil has a yellow colour. The extracted oil, freed by filtration from other ether-soluble substances, was semi-solid and had an orange-yellow colour. The specimen examined by *Kitt* contained 0·2 per cent of lecithin, and 1·5 per cent of cholesterol; its acid value was 1·2.

[1] *Analyst*, 1896, 161. [2] *Chem. Zeit.* 1897, 303.

Physical and Chemical Characteristics of Egg Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 25° C.	Observer.
15	0·9144	Kitt	8-10	Paladino and Toso [1]	22-25	Paladino and Toso	190·2	Kitt	72·1	Kitt	0·4	Kitt	1·4713	Spaeth
20	0·9156	Paladino and Toso					185·2-186·7	Paladino and Toso	81·2-81·6	Paladino and Toso	0·66	Spaeth	Butyro-refractometer. "Degrees."	
100 (water at 15° = 1)	0·881	Spaeth					184·4	Spaeth	68·5	Spaeth			At 25° C.	Observer.
													68·5	Spaeth

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Neutralisation Value.		Iodine Value.		Mean Molecular Weight.	
Per cent.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.		Observer.
95·16	Kitt	34·5-35	Paladino and Toso	194·9	Kitt	72·6	Spaeth	285	Kitt
		36	Spaeth			73·25	Kitt		
		36-39 [2]	Kitt						

[1] *Analyst*, 1896, 161.

[2] Capillary tube method.

Egg oil gives the elaïdin reaction. The acetyl value 11·9 recorded by *Kitt* does not necessarily point to the presence of hydroxylated fatty acids, since even if the number itself were not open to doubt on account of a faulty method having been applied (cp. Vol. I. Chap. VI.), the high amount of cholesterol in the oil conditions a notable acetyl value.

In the commercial determination of the fatty oil in the yolk, the choice of the solvent is by no means irrelevant. *Jean*[1] has shown that by extracting one and the same specimen of dried yolk with the following solvents: petroleum ether, ether, carbon bisulphide, carbon tetrachloride, and chloroform, the following respective proportions of oil were obtained:—48·24 per cent, 50·83 per cent, 50·45 per cent, 50·30 per cent, and 57·66 per cent. Another specimen of yolk was extracted successively with the three solvents: petroleum ether extracted 27·3 per cent of oil; the extraction with ether then yielded 1·05 per cent; the subsequent extraction with chloroform furnished an additional 1·37 per cent. *Vignon* and *Meunieur*[2] recommend chloroform as best suited for the extraction of egg oil. The following results were published by them:—

	Oil. Per cent.	Iodine Value of Oil.	Unsaponifiable Matter. Per cent.	Phosphorus calculated to Phosphoric Acid (PO_4H_3). Per cent.
Hen's egg . . .	32·7	52	0·2	2·33
Duck's egg . .	38·9	37·4	2·7	1·91

The saponification value of egg oil extracted from hen's egg with petroleum ether was 188, and the refractive index at 20·2° C. 1·4655.

Egg oil finds commercial application in the leather industries for "tawing." As regards its employment in tempera painting, cp. German patent 187,211 (*Lupus*).

The terrestrial animal oils from quadrupeds are characterised by low iodine values—lower than those of the non-drying vegetable oils—and by low thermal reactions. They yield solid elaïdins with nitrous acid; chemically, they are readily differentiated from vegetable oils by means of the phytosteryl acetate test.

In addition to the oils obtained from the feet of sheep, horses, and of neat, the liquid fats obtained from lard, horse fat, bone fat, and tallow by pressing would fall under this head. The last-named oils are, however, more suitably described in connection with the raw material from which they are derived.

[1] *Zeit. f. Unters. d. Nahrungs- und Genussm.* 1904, 232.
[2] *Collegium*, 1904, 128, 129.

SHEEP'S FOOT OIL

French—*Huile de pieds de mouton.*
German—*Hammelklauenöl, Schafpfotenöl.*
Italian—*Olio di piede di montone.*

For tables of characteristics see p. 399.

This oil is obtained from sheep's trotters in the manner described under "Neat's foot oil" (see p. 402). The sample examined by the author (see table) was prepared in the laboratory.

Sheep's foot oil much resembles neat's foot oil, and is, as a rule, sold as such. This oil has been adopted by *Amagat* and *Jean* as the standard (*huile type*) for their oleo-refractometer.

Physical and Chemical Characteristics of Sheep's Foot Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·9175	Schaedler	0 to 1·5	Schaedler	194·75 [1]	Lewko-witsch	74-74·4 [1]	Lewko-witsch	49·5	Jean	0 [2]	Jean

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. Titer Test.	
°C.	Observer.
20·0-21·1 [1]	Lewkowitsch

[1] Specimen prepared in the laboratory.

[2] Sheep's foot oil is the standard oil.

HORSES' FOOT OIL

French—*Huile de pieds de cheval.* German—*Pferdefussöl.*
Italian—*Olio di piede di cavallo.*

For table of characteristics see p. 401.

This oil is obtained from horses' feet by boiling them with water.

It is not met with in commerce under its true name, and what is described as horse oil is more or less the liquid portion of horse fat. The horses' feet are usually boiled out together with neat's feet and sheep's feet, and the resulting oil is indiscriminately sold as neat's foot oil, or at least as "animal" oil.

The specimen rendered in the author's laboratory contained, even after filtering, certain impurities, so that the oil gave several colour reactions which were previously considered as characteristic of marine animal oils (cp. p. 334). The oil had a high acetyl value, viz. 9·1-10·3, due to changes caused by contact with organic impurities.

Physical and Chemical Characteristics of Horses' Foot Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Maumené Test.	
At ° C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
15	0·9202-0·9205 0·9270	Jean Amthor and Zink	195·0-196·8	Lewkowitsch	73·7-73·9 90·3	Lewkowitsch Amthor and Zink	38	Jean

Insoluble Fatty Acids :—Solidifying Point (Titer Test) 27·1-28·6° C. (*Lewkowitsch*).

NEAT'S FOOT OIL

French—*Huile de pieds de bœuf.* German—*Ochsenklauenöl, Rinderklauenöl.* Italian—*Olio di piede di bove.*

For tables of characteristics see pp. 404, 405.

Neat's foot oil (*Oleum bubulum* of the British Pharmacopœia) is obtained from the feet of cattle by boiling with water. In this country the preparation of neat's foot oil is chiefly carried out in small establishments, in which the by-products and waste material of the slaughter-houses are worked up ("tripe shops"). The feet are carefully scraped and washed, the hoofs are cut off, and after the hair has been removed they are boiled with water in jacketed pans heated by steam, the water being kept simmering for eight to ten hours. The oil rises to the top, and is skimmed off from time to time by means of suitable skimmers. The oil is then allowed to settle in a warm place, salt being sprinkled on the top to facilitate the separation of the water. Finally, the oil is washed with water, in order to remove any gluey substances, and filtered. On cooling, some "stearine" is deposited. In the production of the best kind of neat's foot oil having a low cold test, the clear oil is decanted off the "stearine." Such decanted oil has a cold test of about 25° to 28° F. The oil prepared in an establishment standing under the author's supervision was obtained in this manner.

On a large scale neat's foot oil is obtained as a by-product in the centres of the meat packing trade, such as in the Chicago stock yards and in the South American establishments. There the feet are taken in their fresh state from the slaughter-houses ("killing-beds"), washed free from adhering blood and dirt, and sawn by a circular saw into suitable sizes for further working up. The chief object of sawing off the feet is to separate the more costly shin bones from the feet proper, which latter yield the genuine neat's foot oil. The fatty matter contained in the shin bones approaches somewhat in consistence horse- or beef-marrow fat (see below), as the case may be. When kept separate it is sold as "bone oil" (French—*Huile d'os*; German—*Knochenöl*). This oil must not be confounded with neat's foot oil, nor with bone fat. It is, however, customary in America to recover the oil from the shin bones, together with the neat's foot oil, by boiling the shin bones with the feet. Therefore, American oil has a higher solidifying point than that prepared as described above. The feet are scalded by immersion in boiling water for from 10 to 15 minutes in order to loosen the hoofs, which are removed by a special machine—the "hoof-puller." The boiling out of the hoof must be avoided, as otherwise some colouring matters contained in the hoof would pass into the oil and

depreciate its value. It will be readily understood that the greatest speed in the working up of the oil is required, as contact with the putrescible animal matter is apt to set up secondary reactions which lead to the production of a low-class oil, containing a high proportion of free fatty acids, and having a dark colour and an unpleasant smell.

The further treatment of the oil is very similar to the one described above. The oil is skimmed off as it rises to the surface, filtered roughly through a fine wire screen, separated from water as far as possible, and then run into vessels provided with close steam coils. Steam is passed through the coils and the water still contained in the oil thereby driven off, whilst at the same time organic impurities (albumen) become coagulated. The dried oil is finally obtained in a perfectly limpid state by filtering.

Neat's foot oil is pale yellow and has a bland taste. Properly prepared oil contains only a very small amount of free fatty acids. On standing the oil deposits "stearine." The glycerides contained in neat's foot oil consist of palmitin, stearin, and olein. Linolin appears to be absent, for *Coste* and *Shelbourn* found amongst the oxidation products of the liquid acids of neat's foot oil dihydroxystearic acid only. The amount of unsaponifiable matter varies from 0·12 to 0·65 per cent.

Commercial samples of European neat's foot oil, even if not sophisticated with non-animal oils, consist mostly of true neat's foot oil mixed with sheep's foot and horses' foot oils. Frequently tallow oil ("animal oil") recovered from greases (see Vol. III. Chap. XVI.) is substituted for neat's foot oil. American neat's foot oil mostly contains the oil from the shin bones, which is, properly speaking, a marrow fat. Hence the solidifying point of American oil lies as a rule above 0° C. The chief determinants in the valuation of the oil are colour, smell, low freezing point, and freedom from free fatty acids.

For the purposes of the leather industries a low "cold-test" is of especial importance, as the finished glazed leather becomes coated with a film of "stearine" in cold weather if neat's foot oil containing a considerable quantity of "stearine" has been used.

The high price of the oil acts as an incentive to fraud. It is largely adulterated with vegetable oils, such as rape oil and cotton seed oil. Fish oils (blubber oils, whale-bone oil) and mineral oils are also used for the same purpose. These adulterants can be easily detected by determining the iodine value. If the amount of added vegetable oils be so small that the indications furnished by the iodine value of the sample, the iodine value of the liquid fatty acids, the saponification value (rape oil), and other chemical or physical tests, do not lead to decisive results, then their presence can be unmistakably ascertained by the phytosteryl acetate test.

Fish oils and blubber oils are best detected by the bromide test; mineral oil is easily determined and identified by examining the "unsaponifiable" matter.

Physical and Chemical Characteristics of Neat's Foot Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·914-0·916	Allen	−3 to −4[6]	Lewkowitsch	194·3[2]	Lewkowitsch	69·3-70·4[2]	Lewkowitsch
15	0·9152-0·9165[1]	Jean	10[1]	Jean	195·5-197·4[3]	Coste and Parry	71·1-72·4[3]	Coste and Parry
15·5 (water at 15·5=1)	0·9169-0·9174[3]	Coste and Parry			196-199[5]	Holde and Stange	66-76[5]	Holde and Stange
15·5	0·9164[4]	Coste and Shelbourn					67·1-72·9[1]	Gill and Rowe
18	0·9142	Stilurell						
99 (water at 15·5=1)	0·8619	Allen						

Physical and Chemical Characteristics of Neat's Foot Oil—continued

Reichert-Meissl Value.		Maumené Test.		Refractive Index.	
cc. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At 20° C.	Observer.
1·0[4]	Coste and Shelbourn	47-48·5	Jean	1·4681[4]	Coste and Shelbourn
		42·2-49·5[1]	Gill and Rowe		
		56-58[3]	Coste and Parry		

Oleo-refractometer.	
"Degrees."	Observer.
−3 to −4 −1 to −3 at 22° C.	Jean Pearmain

Specific Temperature Reaction.	
°C.	Observer.
87·9-103·1[1]	Gill and Rowe

Butyro-refractometer.		
°C.	"Degrees."	Observer.
20	64·2[4]	Coste and Shelbourn

[1] American oil. [2] Oil rendered in the laboratory. [3] Two specimens of oil rendered in the laboratory.
[4] Average of samples rendered in the laboratory. [5] Means of eleven samples of pure oil. [6] Freed from stearine.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	At 100° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
95·3-95·5 [3]	Coste and Parry	0·8742-0·8800 [3] (water at 100° C. = 1)	Coste and Parry	26·1	Coste and Parry	29·8-30·8 [1]	Jean	200·6-201·2	Coste and Parry	61·98-63·26 [1]	Jean
95·2 [4]	Coste and Shelbourn	0·8713-0·8749 [4]	Coste and Shelbourn	Titer Test.		28·5-29·2 [3]	Coste and Parry	202·9-206·3	Coste and Shelbourn	74·5-75·8	Coste and Parry
				26·1-26·5 [2]	Lewkowitsch					71·0-77	Coste and Shelbourn
				16-26·5 [1]	Gill and Rowe					63·6-69·5	

[1] American oil. [2] Oil rendered in the laboratory. [3] Two specimens of oil rendered in the laboratory.
[4] Average of samples rendered in the laboratory.

Neat's foot oil is a valuable lubricating oil for clocks, guns, sewing machines, and other delicate machinery. (A specimen of true neat's foot oil required in *Redwood's* viscosimeter at 140° F., 70 seconds; and at 200° F., 43 seconds.) It is largely used in the leather industry, in which practically the total quantity of neat's foot oil made is consumed as "fat liquoring" for the treatment of hides and skins for the manufacture of the more delicate grades of leather (gloves, etc.).

Dunlop (*Analyst*, 1907, 318) obtained from *calves' feet* a white salve-like fat of the iodine value 71·8, and the refraction 59·0 "degrees" at 25° C. in the butyro-refractometer. The oil filtered from this product at 13·3° C. had the iodine value 74·1.

Horse Oil (see under "Horse Fat").

Lard Oil (see under "Lard").

Tallow Oil (see under "Tallow").

II. SOLID FATS

1. Vegetable Fats

The vegetable fats are obtained from plants widely distributed over tropical and sub-tropical regions. In the world's markets hitherto only a few have acquired considerable commercial importance. These are palm oil and its kernel oil, and cocoa nut oil; cacao butter and Japan wax rank next. There is, however, no doubt that in the near future large quantities of vegetable fats will become available for industrial purposes as the conditions of communication and transport (both by land and sea) with the countries of their origin improve. Tropical Africa (especially tropical West Africa—Nigeria, the French Colonies, and the Soudan), the East Indies, the Sunda Islands, and South Sea Islands, the vast regions of tropical South and Central America are bound to furnish in future large quantities of fats. At present the enormous tracts of French Nigeria, of the Soudan, and of Indo-China are being systematically explored for fruits likely to yield vegetable fats. The Colonial Exhibition held at Marseilles in 1906 is sure materially to assist the efforts that have been made hitherto in French West Africa and Indo-China to foster the trade in vegetable fats.

The vegetable fats are chiefly found accumulated in the seeds. Vegetable tallow of China, however, forms a coating round the seeds; and in the case of palm oil the fruit flesh contains considerable quantities of fat, which differs in its chemical composition from the fat of the seed (palm kernel). Whilst, therefore, the palm fruit would be analogous to the olive fruit, in that it yields a fruit oil and a kernel oil, there is this characteristic difference that olive kernel oil has practically the same composition as the oil from the pulp of the fruit. Ouara oil and ouara kernel oil simulate palm oil completely.

The members belonging to this class are solid in temperate climates. They present, however, a variety of gradations from the soft, buttery mass of laurel oil to the hard, wax-like Japan tallow. As the hardness of the fats increases approximately in direct proportion to the decrease of glycerides of oleic acid and linolic acid, the iodine value would most aptly determine, in the absence of other more striking chemical characteristics, the order in which the individual fats should be enumerated.

I have, therefore, grouped the vegetable fats in the first instance in the order of their iodine values.

Palm nut oil and cocoa nut oil, however, have been placed together as undoubtedly constituting, with mocaya oil, maripa fat, and similar fats, a well-defined group, differing from all other

(*b*) HYDNOCARPUS OIL[1]

French—*Huile de hydnocarpus.* German—*Hydnocarpusöl.*
Italian—*Olio di hydnocarpus.*

For tables of characteristics see p. 411.

Hydnocarpus oil is obtained from the seeds of *Hydnocarpus Wightiana*, Blume, a tree indigenous to the western peninsula of India from South Concan to Travancore. The tree belongs to the same natural order as *Taraktogenos Kurzii*, King (yielding chaulmoogra oil, p. 408), and *Hydnocarpus anthelmintica*, Pierre (yielding lukrabo oil, p. 411). The kernels form 70 per cent of the weight of the total seeds, and yield under hydraulic pressure 32·4 per cent of fat. On completely extracting the comminuted seed with ether 41·2 per cent of fat is obtained.

The fat is, at the ordinary temperature, a soft solid; it has a faintly yellow colour and a characteristic odour. The most characteristic property of the oil is its optical activity; $[\alpha]_D = +57{\cdot}7^\circ$ (expressed oil); $+56{\cdot}2^\circ$ (extracted oil). The rotatory power is due to the presence of hydnocarpic and chaulmoogric (Vol. I. Chap. III.) acids.

The expressed oil had the acid value 3·8; the extracted oil the value 7·4. The unsaponifiable matter of the fat was identified as phytosterol.

The mixed fatty acids are optically active; $[\alpha]_D = +60{\cdot}4^\circ$ (in chloroform). From the mixed fatty acids there were isolated, by crystallisation from alcohol, chaulmoogric acid and its lower homologues, hydnocarpic acid. The acids contained in the alcoholic mother liquor yielded, on distillation under 20 mm. pressure, the following three fractions:—(1) Fraction boiling at 220-225° C. These acids absorbed 129·1 per cent of iodine, and had $[\alpha]_D = +41{\cdot}9^\circ$ (in chloroform). (2) Fraction boiling at 225-230° C. The acids of this fraction absorbed 131·1 per cent of iodine, and had $[\alpha]_D = +46{\cdot}6^\circ$ (in chloroform). (3) Fraction boiling at 230-235° C. These acids absorbed 140·7 per cent of iodine, and had $[\alpha]_D = +50{\cdot}4^\circ$ (in chloroform). The high specific rotatory powers of these fractions point to their containing large proportions of acids belonging to the chaulmoogric series. On the other hand, their high iodine numbers indicate that they contain an acid or acids belonging to the linolic or linolenic series. No palmitic acid could be obtained (difference from chaulmoogra oil).

Hydnocarpus oil has been suggested as a substitute for chaulmoogra oil in its pharmaceutical applications, and has been used in the Bombay Presidency with satisfactory result. The seeds are not yet an article of commerce.

[1] Power and Barrowcliff, *Journ. Chem. Soc.* 1905, 886.

Physical and Chemical Characteristics of Hydnocarpus Oil

Specific Gravity.		Melting Point.	Saponification Value.	Iodine Value.
At ° C.		° C.	Mgrms. KOH.	Per cent.
25	0·958	22-23	207	101·3 [1]
...	...	...	...	102·5 [2]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Iodine Value.
° C.	Mgrms. KOH.	Per cent.
41-44	214·0	106·3

(*c*) LUKRABO OIL [3]

French—*Huile de lukrabo.* German—*Lukraboöl.*
Italian—*Olio di lukrabo.*

For tables of characteristics see p. 412.

Lukrabo oil is the fat obtained from *Hydnocarpus anthelmintica*, Pierre, a tree indigenous to Siam, northern Cochin China, and Camboja.[4] The tree belongs to the same natural order as *Taraktogenos Kurzii*, King (yielding chaulmoogra oil, p. 408), and *Hydnocarpus Wightiana*, Blume (yielding hydnocarpus oil, p. 410). The seeds are exported to China under the name of "Lukrabo" ("krebao" seed of Camboja; Annamite, "Chung-bao," "Chumbao"; Chinese "Dai-phong-tu"). The kernels form 31·2 per cent of the total seeds. On subjecting the seeds to hydraulic pressure an amount of fat equivalent to 16·3 per cent of the entire seeds was obtained. By complete extraction with ether the amount of fat rose to 17·6 per cent. This fat is, at the ordinary temperature, a nearly white solid, having the same characteristic odour as chaulmoogra oil and hydnocarpus oil. Like the two latter fats, it is optically active. *Power* and *Barrowcliff* found $[\alpha]_D = +42{\cdot}5°$ for the expressed oil, and $+51°$ for the extracted oil

[1] Expressed oil. [2] Extracted oil.
[3] Power and Barrowcliff, *Journ. Chem. Soc.* 1905, 886.
[4] Cp. Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, 1902, p. 122.

(in chloroform). The expressed oil had the acid value 7·5, and the extracted oil the acid value 8·1.

The mixed fatty acids form a hard white solid; their specific rotation is $[\alpha]_D = +53{\cdot}6^\circ$ (in chloroform). Amongst the acids were identified chaulmoogric acid, hydnocarpic acid, and palmitic acid. The presence of oleic acid was also ascertained.

Physical and Chemical Characteristics of Lukrabo Oil

Specific Gravity.		Melting Point.	Saponification Value.	Iodine Value.
° C.		° C.	Mgrms. KOH.	Per cent.
25	0·953	24-25° [1]	212	86·4
25	0·952	23-24° [2]	208	82·5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Iodine Value.
° C.	Mgrms. KOH.	Per cent.
42-43	202·5	87·8

PARKIA OIL

French—*Huile de Parkia.* German—*Parkiaöl.*
Italian—*Olio di Parkia.*

This fat is obtained from the seeds of *Parkia africana*, R. Br.[3] (Family, *Mimosaceæ*). A specimen of seeds obtained from Togo [4] (West Africa) showed that they contained 16 per cent of fat and 29 per cent of proteids. The seed kernels yielded 22 per cent of fat and 42 per cent of crude proteids.

The oil obtained from the seeds by extracting with petroleum ether has a golden-yellow colour, and is tasteless and odourless; at the ordinary temperature it is semi-liquid to solid. The following

[1] Expressed oil. [2] Extracted oil.

[3] The fruit pulp of *Parkia biglobosa*, Benth., serves the natives of tropical Africa as a food. The pulp is known as "Netté meal" (A. Goris and L. Crété, *Compt. rend.* 1908 (**146**), 187).

[4] H. Fincke, *Zeit. f. Unters. d. Nahrungs- u. Genussm.* 1907, xiv. 512.

characteristics have been ascertained in a specimen having the acid value 2·5 :—

Saponification value	184·5
Iodine value	91·6
Reichert-Meissl value	0·6
Refraction in Zeiss Butyro-refractometer—	
at 25°	67·2 "degrees."
at 40°	58·8 ,,
Insoluble fatty acids + unsaponifiable .	95·5 per cent.

The kernels are used by the natives of the Soudan in the preparation of the "Daua-Daua" cakes, which are used as a condiment, and also as food. The "Daua-Daua" cakes ("Daua-Daua cheese") are largely sold as an article of commerce in the Soudan markets. The roasted seeds are known as "Soudan coffee."

PONGAM OIL [1]

French—*Huile de pongam ; huile de Hongay.* German—*Pongamöl.* Italian—*Olio di pongam.*

For table of characteristics see p. 414.

This oil is obtained from pongam beans, the fruits of *Pongamia glabra*, Vent. (*Dahlbergia arborea*, Willd. ; *Galedupa arborea*, Roxb.[2]), a tall tree growing all over East India from the Central and Eastern Himalayas to Ceylon and Malacca. The tree occurs also in the Malayan Archipelago, North of Australia, the Pacific Islands, and the Seychelles.

The oil is known under the following native names :—Kanoogamanoo, Kanoogoo, Kanuga-Karra, Kanuga-Chettu ; it is also known as Korung oil and Kagoo oil.

According to *Lépine* (*Pharm. Journ.* (3) xl. 16) the seeds yield 27 per cent of a yellow oil, of the specific gravity 0·945, solidifying at 8° C.[3] The authors of the *Pharmacographia Indica* state (see Watt's *Dictionary of the Economic Products of India*, VI. i. p. 322) that the oil (called Houge oil in Mysore) expressed from fresh seeds was thick, of a light orange-brown colour, and bitter taste (perhaps due to the presence of resinous matter or of an alkaloid). The specific gravity at 18° C. was 0·9458. It yielded 93·3 per cent of fatty acids, melting at about 30° C.

By extracting pongam beans with ether I obtained 33·7 per cent of a buttery mass of a dirty-yellowish colour. I was enabled to examine, side by side with the oil extracted from the seeds, a native specimen obtained from India. This specimen contained 0·5 per cent of free fatty acids (in terms of oleic), and 6·9 per cent

[1] Lewkowitsch, *Analyst*, 1903, 342.

[2] The pongam seeds must not be confounded with the seeds of *Dahlbergia sissoo*.

[3] Cp. Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, p. 86.

of unsaponifiable matter. The sample prepared in my laboratory contained 3·05 per cent of free fatty acids, and 9·22 per cent of unsaponifiable matter.

The oil is used in India for medicinal and illuminating purposes. As it can be obtained in large quantities, it should find technical application in the soap and candle industries.

Physical and Chemical Characteristics of Pongam Oil

Specific Gravity at ° C.		Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer. "Degrees" at 40° C.	Observer.
15 (water at 15°=1)	0·93693[1]					Lewkowitsch
40 (water at 40°=1)	0·9240[1]	183·1[1]	89·4[1]	1·1[1]	70[1]	,,
,,	0·9352[2]	178[2]	94·0[2]		78[2]	,,

The titer test of the insoluble fatty acids was 44·4° C.

LAUREL OIL, BAYBERRY OIL

French—*Huile de laurier.* German—*Lorbeerfett.*
Italian—*Burro di lauro, Olio di lauro.*

For tables of characteristics see pp. 416, 417.

Laurel oil[3] is obtained from the berries of the laurel tree, *Laurus nobilis*, L., either by pressing, or by boiling the pounded berries with water. The berries contain from 24 to 30 per cent of fat. Laurel oil has a green colour. At the ordinary temperature it has a buttery consistence; its taste and aromatic odour are characteristic.

Laurel oil is completely soluble in boiling alcohol; on cooling, crystals of trilaurin separate. Judging from the high iodine value, laurel oil must contain considerable quantities of olein (and perhaps also less saturated glycerides); hence the statement occurring in the older literature on this oil, viz. that the chief constituent of laurel oil is trilaurin, must be considered as erroneous. The quantity of laurin cannot be very high, as is evidenced by the characteristic numbers given in the tables. The presence of laurin is, however, definitively

[1] Specimen obtained from India. [2] Extracted in the laboratory with ether.

[3] Laurel oil must not be confounded with the oil from the seeds of *Calophyllum inophyllum* (see table facing p. 192): specific gravity, 0·9315 at 16° C.; saponification value, 196·4; melting point of insoluble fatty acids, 37·6° C. Nor should laurel oil be confounded with Indian laurel oil (described p. 115), from the fruits of *Laurus indica*.

proved by the following facts :—On distilling laurel oil *in vacuo*, *Krafft* obtained trilaurin in the distillate. *Matthes* and *Sander* found the proportion of insoluble fatty acids (determined by *Hehner's* method) 85·8 per cent after deducting 1 per cent of unsaponifiable matter.

The titration number of the insoluble volatile acids was 2·8, but this would of course not prove the presence of lauric acid (see Vol. I. Chap. VIII.). *Allen* found also small quantities of volatile acids (acetic). A sample examined by the author had the acid value 26·3.

The unsaponifiable matter of laurel oil consists, according to *H. Matthes* and *H. Sander*,[1] of melissyl alcohol, phytosterol (melting at 132-133° C.), a hydrocarbon "laurane," $C_{20}H_{42}$ (crystallising from alcohol in fine needles melting at 69° C.), and an oily substance of brown colour having an ethereal odour, the iodine value 191·95 and n_D at 40° C. = 1·5018. The exceedingly small amount of this oil cannot appreciably affect the iodine value of the oil, and the opinion of *Matthes* and *Sander* that the high iodine value of laurel oil is due to the high iodine absorption of the unsaponifiable matter cannot be admitted as correct. The *true acetyl value* of the oil was found by *Matthes* and *Sander* to be 5·1 ; to the greatest extent this number is due to the presence of higher alcohols in the unsaponifiable matter. The *apparent acetyl value* was 15·3 for the oil having an acid value 9·4.

The numbers given in the table of characteristics are somewhat widely divergent. This must be due to the fact that crude laurel oils contain varying amounts of a volatile oil. In order to separate the latter from the fatty oil *Fabris* and *Settimj*[2] digested crude laurel oil (the characteristics of which are given in the table, p. 416) at a temperature of 0° C. with 95 per cent alcohol, filtered, and washed the undissolved portion with 95 per cent alcohol at a temperature of 0° C. until nothing more was dissolved by the alcohol.

The fat which was insoluble in alcohol had the consistence of tallow, and was colourless and odourless, whereas the (smaller) portion dissolved by alcohol was an oily liquid of a dark green colour and very intense odour. The characteristics of the two portions were as follows :—

	Fat insoluble in Alcohol at 0° C.	Oil soluble in Alcohol at 0° C.
Solidifying point	26-28° C.	...
Melting point	40-50° C.	...
Saponification value	206·5	186·6
Iodine value	65·6	124·1
Insoluble fatty acids + unsaponifiable	90·0 per cent	...
Butyro-refractometer "degrees" at 40° C.	53	85

[1] *Arch. der Pharm.* 1908 (246), 165.

[2] *Atti del VI. Congresso internazionale di Chimica applicata*, Roma, 1907, v. 753.

Physical and Chemical Characteristics of Laurel Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·93317	Cloëz	24	Villon	33-36	Villon	198·9	Allen
15	9·953	Fabris and Settimj	24-25	Fabris and Settimj	32-33	Fabris and Settimj	197·5	Fabris and Settimj
98·5 (water 15·5=1)	0·8806	Allen	25	De Negri and Fabris	32-34	De Negri and Fabris	197·5	De Negri and Fabris
							197·7-198·1	Lewkowitsch
							197-210	Morpurgo
							200·9	Matthes and Sander

Physical and Chemical Characteristics of Laurel Oil—continued

Iodine Value.		Reichert Value.		Butyro-refractometer.		Maumené Test.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	"Degrees."	Observer.	°C.	Observer.
67·8	De Negri and Fabris	1·6	Allen	80 (at 25° C.)	Fabris and Settimj	115·6	Fabris and Settimj
96·4	Fabris and Settimj			72 (at 40° C.)	,,		
80·4-80·5	Lewkowitsch	Reichert-Meissl Value.		Refractive Index.			
75-78·4	Wijs						
66-78	Morpurgo	3·2	Matthes and Sander	At 40° C.	Observer.		
82·3	Matthes and Sander	5·4	Fabris and Settimj	1·4643	Matthes and Sander		

The insoluble fatty acids from the alcohol-insoluble fat gave the following numbers :—

Solidifying point	18-19° C.
Melting point	23-24° C.
Iodine value	64·7
Iodine value of the liquid fatty acids . .	98·1

The insoluble acids consisted of equal parts of solid and liquid acids (determined by the lead-salt-ether method).

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.		Solidifying Point.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	Per cent.	Observer.
86·8	Matthes and Sander	Titer Test.			
83·5	Fabris and Settimj	14·3-15·1	Lewkowitsch	81·6-82·0	Lewkowitsch

On shaking laurel oil with twice its volume of alcohol and filtering, a green filtrate is obtained. Hydrochloric acid converts the colour to a yellowish-green which is not changed by ammonia (*Morpurgo*).[1]

Crude laurel oil gives in the *Baudouin* test a colour reaction similar to, although distinct from, that given by sesamé oil. The alcohol-insoluble fat shows the colouration less distinctly, whereas the alcohol-soluble portion gives a very intense colour reaction (*Fabris* and *Settimj*).

Laurel oil is only used in veterinary practice. It is stated to be adulterated with other fats (lard), coloured green with copper salts. Lard would be detected by the isolation of cholesterol; copper, by incinerating the oil and examining the ash.

CARAPA OIL, CRAB WOOD OIL, ANDIROBA OIL, TOULOUCOUNA OIL

French—*Beurre (huile) de Carapa ; huile de touloucouna.*
German—*Carapafett, Tulucunafett.* Italian—*Olio di Carapa.*

For table of characteristics see p. 418 (see also Appendix).

This fat is expressed from the seeds of several species of plants belonging to the genus *Carapa* (Meliaceæ), as *Carapa guianensis*, Aubl.; *Carapa moluccensis*, Lam.; *Carapa procera*, D. C.; *Carapa touloucouna*, Guill. et Perr.

[1] *Giorn. di Farm. di Trieste*, 1905, 353.

Physical and Chemical Characteristics of Carapa Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·912	Milliau [1]	26	Hannau [3]	31	Hannau	195·6	Deering	72·1	Hannau	2·2 [5]	Deering
15·5	0·9225	Deering [2]							65 [4]	Deering		

[1] *Corps gras ind.* 1899, 129.
[2] *Journ. Soc. Chem. Ind.* 1898, 1156.
[3] *Annali del Laboratorio delle Gabelle*, 1891-1892, p. 271.
[4] Calculated by the author from the bromine value 41.
[5] Calculated by the author from Deering's analytical data; volatile fatty acids equivalent to 0·25 per cent KOH.

The percentages of insoluble fatty acids + unsaponifiable were found by *Deering* and *Milliau* to be 93·7 and 95·5 respectively.

The information given in the literature on carapa oil is of a very indefinite nature. This is caused to a great extent by the conflict of opinions of the several botanists who have given descriptions of the carapa plant. Thus the *Carapa guineensis*, Sweet, or *C. touloucouna*, Guillemin et Perrot, has been described as a separate species, differing from the *C. guianensis*, Aubl., which grows abundantly in Guiana and especially in French Guiana. Several botanists consider the South American and West African species as identical, especially so *Oliver*,[1] who declares the botanical differences, on the strength of which *A. Jussieu*, *Richard*, and others discriminated two species, as too unimportant to call for such a subdivision. The difference would seem to be based on the subdivision[2] of the carapa plants into (1) *Peniamera*, with peduncled flowers and parts in fives, and (2) *Tetramera*, with sessile flowers and parts in four. In the former are included *C. procera* and *C. surinamensis*, in the latter *C. guianensis* and *C. moluccensis*. *C. guianensis* and *C. touloucouna* are given in the Kew Index as synonyms for *C. procera*, D.C., and according to a communication on this subject received recently at the Imperial Institute from Kew, *C. guianensis* is *C. procera*.[3]

The natives of Guiana prepare the oil by boiling the kernels with water, and placing them in a heap for a few days, when the mass is triturated in a wooden mortar or between stones. The pulp is then exposed to the sun in an inclined position, so that the exuding oil can drain off. A more advanced process is to boil the mass.

A specimen from Trinidad, examined by *Deering*, had the acid value 22·6; the melting point of the insoluble fatty acids was 38·9° C. The numbers hitherto published are collated in the table, p. 418 (see Appendix).

Chateau[4] discriminated as two separate oils "Carapa oil" (from *C. guianensis*) and "Touloucouna oil" (*C. touloucouna*). This distinction had been emphasised by *Heckel*.[5] In the following tables I collate the numbers given by him:—

	Carapa Seeds.	Touloucouna Seeds.
	Per cent.	Per cent.
Shells	24	28·75
Kernels	66	71·25

[1] *Flora of Tropical West Africa*, vol. i. p. 336. Cp. Semler, *Die tropische Agrikultur*, vol. ii. p. 451.

[2] Cp. Drabble, *Quarterly Journal Institute of Commercial Research in the Tropics* (Liverpool University), vol. iii. No. 6, p. 21.

[3] Lewkowitsch, *Analyst*, 1903, 184.

[4] *Les corps gras industriels*, Paris, 1863, p. 293.

[5] *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, 1902, pp. 141-153.

[TABLE

	Carapa Oil.	Touloucouna Oil.
Yield of oil from the total fruit	24·60 per cent	43·46 per cent
Specific gravity at 15° C.	...	0·932
Maumené test	34° C.	30° C.
Yield of fatty acids by "saponification process"	94·9 per cent	93·27 per cent
Solidifying point of these acids	36·2° C.	32·65° C.
Yield of fatty acids by distillation process	86·3 per cent	83 per cent
Solidifying point of these acids	39·2° C.	39° C.
Yield of solid fatty acids by "saponification process"	43 per cent	27·25 per cent
Solidifying point of these acids	53° C.	51° C.
Yield of solid fatty acids by "distillation process"	49·28 per cent	48 per cent
Solidifying point of these acids	49° C.	48° C.
Yield of glycerin	9·3 per cent	10·58 per cent

These numbers evidently refer to experiments carried out on a manufacturing scale in candle works. The differences shown do not, however, in the author's opinion, establish a definite distinction between the two oils, and in view of the uncertainty attaching to the origin and to the original condition of the fats, especially having regard to the conflict of opinions on the part of expert botanists, the author does not consider that there is sufficient justification for considering "carapa oil" and "touloucouna oil" as two different individuals. Moreover, the name "touloucouna" seems to be, if not a corruption of the name, at least of the same origin as that of *talloconah*, a native name in British Guiana for the carapa tree,[1] known there also as "crab" and "corap."

Lately *Dawe* (of the Forestry Department) discovered a new species of *Carapa*, which has been named *Carapa grandiflora*, Sprague. The author received a considerable quantity of the nuts for examination from the Imperial Institute, and examined the oil obtained from them.

Oil from Carapa Grandiflora[2]

A large portion of the kernels were mouldy, and in several lots of nuts amounting to about 10 pounds each the good kernels and shells were determined quantitatively with the following result:—

Good kernels, 36·3 to 42·1 per cent; bad kernels, 25 to 22·3 per cent; shells, 38·7 to 35·6 per cent. The good kernels yielded, on extraction with ether, 30·26 per cent of oil.

The large quantity at my disposal permitted the preparation of cold-pressed oil, hot-pressed oil, and cake on a semi-large scale. For the preparation of the hot-pressed oil good kernels were selected, comminuted in a manner simulating the operations on a large scale,

[1] Malonay, *Sketch of the Forestry of West Africa*, p. 296.
[2] Lewkowitsch, *Analyst*, 1908, 186.

and expressed in the cold in a hydraulic press at a pressure of 150 atmospheres. The amount of cold-pressed oil so obtained was over 10 per cent of the raw material. The cold-pressed cakes were then broken up, comminuted, and heated to 150° F., when they were again expressed in the hot press at a pressure of 150 atmospheres. Thus a further quantity of hot-pressed oil, amounting to almost double the quantity obtained by cold expression, was recovered. Quantitative recovery of the oil was, of course, out of the question, and the cakes finally obtained contained much more oil than would be left in a commercial oil cake.

The cold-pressed oil as also the hot-pressed oil were examined side by side, with the result set out below. The colour of the cold-pressed oil is almost white with a tinge of pale yellow; at the ordinary temperature it solidifies. The hot-pressed oil is much darker in colour, and remains solid at the ordinary temperature. The following characteristics were ascertained :—

Oil.	Cold pressed.	Hot pressed.
Specific gravity at 40° C. (water at 40=1)	0·9171	0·9215
Specific gravity at 15·5° C. (water at 15·5=1)	0·9261	0·9306
Solidifying point	8° C.	10° C.
Melting point	15-23° C.	20-30° C.
Saponification value	198·1	201·8
Iodine value	83·7	72·6
Reichert-Meissl value	3·75	3·83
Unsaponifiable matter	3·75 %	1·59 %

Insoluble Fatty Acids.	Cold pressed.	Hot pressed.
Fatty acids + unsaponifiable	94·03 per cent	92·93 per cent
Solidifying point (Titer test)	34·9° C.	38·9° C.
Neutralisation value	202·3	202·4
Mean molecular weight of the fatty acids	277·3	277·1

The insoluble fatty acids consisted of :—

	Cold pressed.	Hot pressed.
"Liquid" acids (yielding ether-soluble lead salts)	72·82 per cent	64·62 per cent
"Solid" acids (yielding ether-insoluble lead salts)	26·47 per cent	34·93 per cent
Iodine value of liquid fatty acids	94·74	94·71
Iodine value of solid fatty acids	8·8	9·97
"Solid" acids yielded "stearic acid," melting point 65·6° C.	3·15 per cent	6·6 per cent

The cold-pressed oil rotated the plane of polarised light 2° 4′ to the left in a 100-mm. tube (the rotation is very likely due to the presence of a resin).

The oils as also the cake have an intensely bitter taste, which seems to be characteristic of all the oils derived from the seeds of the *Carapa* family. Hence the oil is unfit for edible purposes. Carapa oil is used in Brazil, Guiana, the West Coast of Africa, India, and the Moluccas as an ointment, to protect the natives against the attacks of insects, and for burning purposes. The statement that carapa oil is exported from South America into England and France for soap-making purposes requires confirmation. From notes occurring in the literature on this subject, and from private information given to the author, it appears that seed from *C. touloucouna* was expressed in Marseilles on an experimental scale some time ago, but at present no seeds are being imported into France. The cake so obtained was stated to contain a considerable amount of proteids, viz. 27·3 per cent. The commercial value of the kernels must depend upon the use that can be made of the cakes. If the bitter principle in the cakes precludes their use as cattle food, they can only be sold as manure, and their value would then be low.

NUX VOMICA FAT

French—*Huile de noix vomique.* German—*Strychnusöl, Brechnussöl.* Italian—*Olio di noce vomica.*

For tables of characteristics see p. 423.

This fat is obtained from the seeds of *Strychnos nux vomica*, L., by extraction with ether. The alkaloids strychnine and brucine which form 3·18 per cent of the crude fat (*Schroeder*[1]) are extracted together with the fat; they are removed by washing the crude extract with dilute acid. The yield of fat from the seeds is about 4 per cent (*Harvey* and *Wilkie*[2]), 4·2 per cent (*Schroeder*).

The fat is slightly fluorescent in its melted state; it has a yellowish-brown colour, an unpleasant but not bitter taste, and a characteristic odour. The fat, prepared as above described, contains a considerable amount of unsaponifiable matter; 12-12·4 per cent (*Harvey* and *Wilkie*), 16·93 per cent (*Schroeder*). In agreement herewith the saponification value is low. The solid fatty acids determined in one specimen amounted to 24·2 per cent, and the liquid acids to 58·4 per cent (*Harvey* and *Wilkie*). According to *Schroeder* the fat contains 8·6 per cent of solid glycerides (palmitin and arachin) and 74·5 per cent of olein.

[1] *Archiv der Pharm.* 243 (1905), 635.
[2] *Journ. Soc. Chem. Ind.* 1905, 718.

Physical and Chemical Characteristics of Nux Vomica Fat

Specific Gravity.		Melting Point.	Saponification Value.	Iodine Value.	Reichert-Wollny Value.	Acetyl Value.	Observer.
°C.		°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.		
100 (water 15·5°=1)	0·8638	Softens at 29 Clear at 31·2	168·9-170·6	73·8-79·3	0·7-1·33	11·68	Harvey and Wilkie
20	0·8826	Clear at 28	166·2[1]	69·4[1]	1·7	42·23	Schroeder

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Mean Molecular Weight.	Iodine Value of the Liquid Fatty Acids.	Observer.
95·2	281·2	94·0-96·2	Harvey and Wilkie
94·9	...	...	Schroeder

[1] Before removal of the alkaloids the saponification value was found to be 160 and the iodine value 64·2.

The unsaponifiable matter of the specimen examined by *Harvey* and *Wilkie* had the iodine value 89·1, so that the iodine value of the true fat would be somewhat lower than 73·8. The acetyl value of the unsaponifiable matter was found to be 105·9, and had the specific rotation in chloroform solution + 39°. (As phytosterol is lævorotatory, there must be present a substance of high dextrorotatory power.)

BAOBAB OIL—RENIALA OIL—FONY OIL

French—*Huile de baobab ; huile de reniala ; huile de fony.*
German—*Baobaböl ; Affenbrotbaumöl.* Italian—*Olio di baobab.*

Physical and Chemical Characteristics of Baobab Oil

Source.	Specific Gravity at 15° C.	Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Observer.
Adansonia digitata . .	0·915	+3 to −3	...	191·7	...	Suzzi
				191·5 [1]	77·8 [1]	Bontoux
				190·5 [2]	76·7 [2]	,,
Adansonia grandidieri .	0·9187	13	24	...	56·8	Milliau
		11-12	24-25	190·9 [1]	55·0 [1]	Bontoux
				189·9 [2]	53·9 [2]	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Source.	Insoluble Acids + Unsaponifiable. Per cent.	Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.	Iodine Value. Per cent.	Observer.
Adansonia digitata .	...	34-32	35·5-38·5	197·5	...	Suzzi
	95·8	...	...	...	...	Bontoux
Adansonia grandidieri .	...	43·2	55	...	...	Milliau
	95·5	44·2	...	...	...	Bontoux
					Liquid Fatty Acids.	
					97·6	Milliau

[1] Expressed oil. [2] Extracted oil.

Baobab oil is obtained from the seeds of various trees belonging to the genus *Adansonia*, in especial from *Adansonia digitata*, L., a tree widely distributed over tropical Africa; *A. Zaha*, Baillon; *A. madagascariensis*, Baillon, known as *Reniala*; *A. grandidieri*, Baillon, known in Madagascar as *Fony*; *A. gregori* (Australia). The shape and the size of the fruits of the different species and their seeds, and the proportions of fat contained in them, vary considerably. Thus *Balland*[1] obtained from kernels brought from Madagascar 63·2 per cent of a fat melting at 24° C. Seeds obtained by *Suzzi* in Erythrea (Italian East Africa) were smaller and contained much less glycerides. Whereas the seeds examined by *Balland* gave 36·7 per cent of shells, *Suzzi's* specimens yielded only 20 per cent. The whitish pulp contained in the Madagascar seeds yielded by expression 39·02 per cent of fat (*Milliau*[2]). *Suzzi*[3] obtained from the kernels of the Erythrean seeds 32·7 per cent of fat of an oily consistence.

A more complete survey of the difference presented by the various seeds of *Adansonia* species is given in the following table, due to *Bontoux*[4]:—

Source.	100 Seeds weigh (Grams):	Shells. Per cent.	Kernels. Per cent.	Proportion of Fat in	
				Kernels. Per cent.	Whole Seed. Per cent.
Adansonia digitata (Senegal) .	45·2	59·2	40·8	30·7	12·5
Adansonia Zaha (Madagascar) .	48·5	52·2	47·8	34·3	16·4
Adansonia madagascariensis (Madagascar) . . .	78·0	44·8	55·2	60·5	34·4
Adansonia grandidieri (Madagascar)	117·0	32·8	67·2	63·5	42·6

The expressed oil has a golden-yellow colour and a pleasant taste; the "Fony oil" in especial has a very pleasant nutty taste. The fats extracted with carbon bisulphide have a red colour, which seems to be due to traces of sulphur contained in the solvent, for in the *Halphen* test (see "Cotton Seed Oil," p. 162) all the oils gave a strong colouration, much more intense than that obtained with cotton seed oil.

[1] *Journ. de Pharm. et de Chimie*, 1904 (20), 529.

[2] *Comptes rendus*, 1904 (134), 808. *Agriculture pratique des pays chauds*, 1904, p. 658.

[3] *I semi oleosi e gli oli*, published for the Milan Exhibition, 1906.

[4] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires, traduit par E. Bontoux*, Paris, vol. ii.

MARGOSA OIL[1]

(VEEPA OIL, VEPPAM FAT, NEEM OIL)

French—*Huile de margosa ; huile de margosier.* German—*Margosaöl.*
Italian—*Olio di margosa.*

This oil is obtained from the seeds of *Melia Azadirachta*, L.[2] (*Azadirachta indica*, Juss.), a large tree, 40 to 50 feet in height, common in the wild or (more often) cultivated state throughout the greater part of India and Burma.

The oil has been described somewhat fully in the *Pharm. Journ.* by *Warden* (see Watt's *Dictionary of the Economic Products of India*, vol. v. p. 211).

The specimen of fat examined by the author was solid at the ordinary temperature. The titer test of the insoluble fatty acids was 42° C.

Physical and Chemical Characteristics of Margosa Oil

Specific Gravity.		Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.	Observer.
At ° C.					Butyro-refractometer at 40° C.	
					"Degrees."	
16 (water at 16° = 1)	0·91423	196·9	69·6	1·1	52	Lewkowitsch
40 (water at 40° = 1)	0·9023					

NIAM FAT[3]

French—*Beurre de Méné (Meni) ; graisse de Niam.*
German—*Niamfett.* Italian—*Grasso di Niam.*

Niam fat is obtained from the fruits of *Lophira alata*, Banks, a tree indigenous to Senegambia, Sierra Leone, and the Egyptian Soudan, and growing profusely along the West Coast of Africa from the Senegal to the Congo. Specimens of undecorticated seeds, produced in Sierra Leone, were submitted to the author by the Imperial Institute, together with a sample of oil extracted from the kernels by the natives in the Egyptian Soudan.

[1] Lewkowitsch, *Analyst*, 1903, 342.
[2] This must not be confounded with *Melia Azedarach*, L.
[3] Cp. also Lewkowitsch, *Journ. Soc. Chem. Ind.* 1907, 1265.

The fruits from Sierra Leone consisted of 61·5 per cent of kernels and 38·5 per cent of husks. (Fruits from the Gaboon and the Congo gave *Heckel*[1] 37 per cent of husks and 63 per cent of kernels.) On extracting the kernels with ether there was obtained, together with the fat, a black resinous mass, which separated out from the oil on evaporating off the ether. This black resinous matter amounted to 0·8 per cent of the weight of the kernels. The fat freed from the black resinous matter formed 31·19 per cent of the kernels. The fat furnished by the whole seeds amounts, therefore, to 19·18 per cent. It represents, at the ordinary temperature, a soft buttery mass, melting at 24° C.

The following characteristics of the fat extracted from the kernels, and also of the fat prepared by the natives of the Egyptian Soudan, were determined in the author's laboratory :—

	Fat extracted from Kernels.	Fat prepared by Natives.
Specific gravity at 40° C. (water at 40 = 1)	0·9105	0·9063
Acid value	18·54	5·78
Saponification value . .	195·6	190·1
Unsaponifiable matter . .	1·49 per cent	1·38 per cent
Iodine value	68·4	78·72
Mean molecular weight of the fatty acids	...	283·7
Solidifying point of the fatty acids (Titer test) . .	...	42·5° C.

Edie[2] resolved the insoluble fatty acids by the lead-salt-ether method into solid acids, having the neutralisation value 195 and the iodine value 22·5, and liquid fatty acids, having the neutralisation value 196 and the iodine value 134·5.

In West Africa this fat is known as "Niam fat" or "Meni oil." It seems preferable to adopt the name Niam fat.[3] The fat has an unpleasant taste, due probably to the small quantity of dissolved resin. Nevertheless, the natives use it for culinary purposes; it is also used as a hair oil.

KADAM SEED FAT[4]

French—*Beurre de Kadam.* German—*Kadamsamenfett.*
Italian—*Burro di semi di Kadam.*

This fat is obtained from the seeds of *Hodgsonia* (*Trichosanthes*) *Kadam*, Miq., a climbing plant belonging to the *Cucurbitaceæ*, and occurring in Padang (Sumatra).

[1] *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, p. 161.
[2] *Quart. Journ. Inst. Comm. Research in Tropics* (Liverpool University), 1907, 2, 124.
[3] Cp. Schweinfurth, *Botan. Ergeb. der ersten Niam-Niam Reise.*
[4] Sack, *De Indische Mercuur*, 1903, 28 (April).

Kadam seed fat is prepared by cutting the fruit into pieces, drying in the sun for a couple of days, and then expressing in bags.

The fat has, at the ordinary temperature, the consistence of butter; it is yellow, non-drying, and odourless. It consists of 80 per cent of triolein and 20 per cent of tripalmitin.

Specific Gravity.		Melting Point.		Saponification Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·919	Sack	21	Sack	197·6	Niederstadt [1]	68·96 [2]	Sack [3]
						66 [1]	Niederstadt

INUKUSU OIL [4]

This oil is obtained from the fruit of *Machilus Thunbergii*, S. et Z., a tree belonging to the *Lauraceæ*, and known in Japan by the name Tabu-no-ki. The fruits are about 0·8 cm. in diameter and weigh about 0·22 grm. each. The specimens examined contained 4·28 per cent of moisture and 65·09 per cent of oil, and yielded 1·3 per cent of ash. The oil has a brownish colour; at low temperatures "stearine" is deposited. The oil gave the following characteristics:—

Specific gravity at 25° C.	0·9347
Acid value	19·31
Saponification value	241·39
Iodine value (*Wijs*)	66·08 per cent.
Refractive index at 25° C.	1·4646
Reichert-Meissl value	2·05

MOWRAH SEED OIL, MOHWRAH BUTTER, MAHUA BUTTER

French—*Huile de Mohwrah, Huile de Mahwrah.* German—*Mowrah-butter, Mahwhabutter, Bassiaöl.* Italian—*Burro di Mowrah.*

For tables of characteristics see pp. 430, 431.

Mowrah seed oil is the fat obtained from the seeds of *Bassia latifolia*, Roxb. = *Illipé latifolia* (Roxb.), Engler = *Bassia villosa*,

[1] Fat obtained from Brazil.

[2] Calculated by the author from the numbers given in the original paper.

[3] Sack, *De Indische Mercuur*, 1903, 28 (April).

[4] Tsujimoto, *Journ. College of Engineering*, Tokyo, 1908, 87.

Wall.,[1] a tree widely distributed in the Northern Provinces of India, and especially in Bengal. It is frequently cultivated in East India. This tree gradually disappears towards Calcutta, and is only sparingly met with in the Madras Presidency, its place being taken by *Bassia longifolia* (see p. 431). It should be noted that in India the Mahua or butter tree is also known as "Illipe butter tree," the vernacular names being (amongst many others) *Illipi, Elupa, Kat illipi.* The seeds contain 50-55 per cent of fat. In the fresh state the fat is yellow, on exposure to the air the colouring matter is bleached. The oil can also be bleached chemically, as has been done by the author on a large scale by a special process.

Mowrah seed oil has a bitter aromatic taste, and a characteristic odour recalling that of cacao beans. The commercial samples contain considerable quantities of free fatty acids, the crystals of which can be recognised under the microscope. The chief constituent of the solid fatty acids is palmitic acid. A number of samples examined in the author's laboratory contained 17·2-20 per cent of free fatty acids (cp. also *Crossley* and *Le Sueur's* numbers below). A specimen examined in the author's laboratory contained 2·34 per cent of unsaponifiable matter.

Crossley and *Le Sueur* have examined a number of genuine specimens, obtained from official sources in India, where this fat is largely used for edible purposes. Their results are reproduced in the following table :—

No.	Origin.	Specific Gravity at 100° C. (Water 100° C. = 1.)	Melting Point. °C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable.	Butyro-refracto-meter. "Degrees."	Viscosity.	
										Seconds at 140° F.	Compared with water.
1	Bengal	0·8975	24·5	11·79	194·00	62·11	0·44	94·95	..	97·1	4·24
2	,, ...	0·8962	26·0	19·15	192·60	64·88	..	..	51·8	93·8	4·10
3	Madras	0·8981	25·0	10·33	191·80	67·85	..	..	..	96·9	4·23
4	,, ...	0·8970	26·5	4·83	190·90	58·53	..	..	..	107·0	4·67
5	,, ...	0·8964	29·0	8·67	187·40	58·45	..	94·69	..	100·6	4·39
6	North-West Provinces .	0·8969	23·0	21·20	189·50	63·51	..	..	..	93·9	4·10
7	Central Provinces . .	0·8971	24·0	17·05	188·80	63·01	..	..	..	96·7	4·22
8	Calcutta	0·8943	25·5	70·82	193·20	58·59	0·88	..	..	90·4	3·95
9	Bombay	0·8980	24·0	6·83	190·50	53·43	..	..	52·4	96·9	4·25

Mowrah seed oil is an important article of commerce. In India it is employed for various technical purposes, and under the name *Dolia oil* fills the place of tallow where the religious tenets forbid the employment of the latter. Under the name *Me oil* it is applied externally in the treatment of skin diseases. Mowrah seed oil is imported from India into this country and into France; it is used in candle and soap making. The mowrah seed cakes are poisonous and can only be used as manure.

[1] Cp. *Les Végétaux utiles de l'Afrique tropicale française*, fascicule ii., par Em. Perrot. Paris, 1907.

Physical and Chemical Characteristics of Mowrah Seed Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.
15 100 (water 100° C. = 1)	0·9175 0·8943-0·8981	Valenta[1] Crossley and Le Sueur	17·25-18·5 19-22	Valenta De Negri and Fabris	25·3 28-31 23-29	Valenta De Negri and Fabris Crossley and Le Sueur	192·3 190·9 190·8-192·4 187·4-194·0	Valenta De Negri and Fabris Lewkowitsch Crossley and Le Sueur

[1] *Dingl. Polyt. Journal*, 251, 461.

Physical and Chemical Characteristics of Mowrah Seed Oil—continued

Iodine Value.		Reichert-Meissl Value.		Refractive Index.		Viscosity.	
Per cent.	Observer.	cc. $\frac{1}{10}$ norm. KOH.	Observer.	At 40° C.	Observer.	Seconds at 140° F.	Observer.
60·4 62·2-63·9 53·43-67·85	De Negri and Fabris Lewkowitsch Crossley and Le Sueur	1·66 0·44-0·88	Lewkowitsch Crossley and Le Sueur	Butyro-refractometer. "Degrees." 51·8-52·4	 Crossley and Le Sueur	90·4-107	Crossley and Le Sueur

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Per cent.	Observer.
94·76 94·69- 94·95	Valenta Crossley and Le Sueur	38	Valenta	39·5	Valenta	56·6	Lewko-witsch

ILLIPÉ BUTTER

French—*Beurre d'Illipé.* German—*Illipébutter.*
Italian—*Burro di Illipe.*

For tables of characteristics see p. 432.

Illipé butter is obtained from the seeds of *Illipe malabrorum*, König. = *Bassia longifolia*, L.,[1] a tree indigenous to the southern part of India and especially the Malayan States. In the south of India this tree is known as the Mowa, or Mahua, or Mahwa tree, the vernacular names being (amongst many others) *Illipi*, *Elupa*, *Ellupi*, *Ilupai*. The commercial Illipé butter is frequently a mixture of true Illipé butter with Mowrah seed oil, the fat from *Bassia latifolia* (cp. p. 428). In Ceylon the oil is known as Me oil. The cake obtained there by pressing the seeds is exported to the coast under the name "arappo."

The seeds are large and more rounded than those of *B. latifolia*. They contain 50-55 per cent of fat. The following yields are obtained on a commercial scale from the brands named :—

Siack[2]	43 per cent.
Singapore	43 ,,
Balan	52 ,,
Pulghéres	32 ,,

In the solid state the oil has a yellow colour; in the melted state the tint varies from yellow to orange. Its odour resembles that of cacao beans.

Blumenfeld and *Seidel* found in a specimen of Illipé butter 1·43 per cent of volatile fatty acids.[3]

Illipé seeds are imported into France and England, where their fat is used in candle-making. According to *Sachs*,[4] Illipé butter is also employed as a chocolate fat. The cake is poisonous and can only be used as manure.

[1] *Les Végétaux utiles de l'Afrique tropicale française*, fascicule ii., par Em. Perrot. Paris, 1907.

[2] Cp. "Borneo Tallow," below.

[3] *Mitth. d. k. k. technolog. Gewerbemuseums*, 10, 160.

[4] *Chem. Revue*, 1908, 8.

Physical and Chemical Characteristics of Illipé Butter

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
36	De Negri and Fabris	42	De Negri and Fabris	188·4	De Negri and Fabris	50·1	De Negri and Fabris

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.
94·76	Valenta	40 39·7-40·3 (Titer)	De Negri and Fabris Lewkowitsch	45	De Negri and Fabris

CHAMPACA FAT

French—*Beurre de Champaca.* German—*Champacafett.*

This fat is obtained in the Dutch Indies from *Melia Champaca.* It is stated by *Sack*[1] to consist of 70 per cent of triolein and 30 per cent of tripalmitin.

Physical and Chemical Characteristics of Champaca Fat

Specific Gravity.	Melting Point. °C.	Iodine Value.
0·903	44-45	60·25[2]

SHEA BUTTER, BAMBUK BUTTER, KARITÉ OIL, GALAM BUTTER

French—*Beurre de Karité,*[3] *Beurre de Cé,*[3] *Beurre de Shée,*[3] *Huile de Karité.* German—*Sheabutter, Galambutter.* Italian—*Burro di Seha.*

For tables of characteristics see p. 433.

This fat is obtained from the seeds of *Bassia Parkii,* De C. (*Butyrospermum Parkii* (G. Don) Kotschy), a tree belonging to the *Sapotaceæ.*[4]

[1] *Indische Mercuur,* 1903, April 28.

[2] Calculated by the author from the percentage of olein.

[3] The name "Karité" is the vernacular with the Onoloff and Touconleur tribes, whilst the Bambaras and Malinke tribes term it Cé or Sé.

[4] Cp. *Les Végétaux utiles de l'Afrique tropicale française,* fascicule ii., par Em. Perrot. Paris, 1907.

Physical and Chemical Characteristics of Shea Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9175	Valenta	17-18	Valenta	28	Allen	192·3	Valenta	56·2-56·9	Lewkowitsch
„	0·9177	Milliau			23-23·3	Stohmann	171·8[1]-187·2	Lewkowitsch	67·2	Milliau
98-99 (water 15·5=1)	0·859	Allen			25·3	Valenta	182·4	Kassler		
							179·0-181·7	Imperial Institute	54-59·4	Imperial Institute

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
94·76	Valenta	38	Valenta	39·5	Valenta	56-57·2	Lewkowitsch
		52·5	Milliau	56	Stohmann	55·6	Kassler
				56·5	Milliau		
		Titer Test.					
		53·8	Lewkowitsch				
		48·6	Kassler				

[1] The unsaponifiable matter in this sample amounted to 9·7 per cent.

The karité tree, resembling in appearance the American oak and growing to a height of about 40 feet and having a massive trunk, occurs in enormous quantities on the West Coast of Africa, in the French and English Soudan. It is especially widely distributed in the middle basin of the Niger, and is as characteristic of the regions of the middle Niger as is the palm tree of the lower reaches of the river and of the coast line. Owing to the wide distribution of the tree, from the West Coast of Africa to the Egyptian Soudan, the different specimens of nuts and fats exported to Europe show some characteristic differences, as the author has ascertained by examining a large variety of shea nuts. The tree growing in the Nile basin appears to constitute a special variety which is known as *niloticum*; the Dahomey tree is described as var. *Poissonii*, whilst the most widely distributed tree is known as var. *mangifolium*. The distinction made in commerce between shea nuts and karité nuts does not appear to be substantiated by an actual difference in the nuts, as the Lagos shea nuts exported into the French colonies are re-exported under the name karité nuts. Although shea butter has been known for a long time, the first specimens of the nuts having been brought home by *Mungo Park*, the first shipment on a commercial scale came to Europe only in 1877. Some attention is at present being paid to the commercial exploitation of shea butter. According to the Colonial Report on Southern Nigeria (Lagos) 25 tons of shea butter were exported in 1904, whereas in 1905, 131 tons were brought by railway from the up-country. In 1906 there were exported 1364 tons of shea nuts (valued at £12,118) and 363 tons of shea butter (valued at £6000). The bulk of this is shipped to the French West African colonies.

At the Colonial Exhibition at Marseilles, 1906, large quantities of shea butters from different regions (Upper Senegal and Niger, French Guinea, and Dahomey) were exhibited. Specimens illustrating shea nuts and shea butters from South Nigeria were exhibited at the Franco-British Exhibition at London, 1908.

The nuts have the size and shape of an ordinary plum. The outer shell of some specimens is covered with fine fibres, whereas the shell of nuts coming from the middle Niger district proper presents the appearance of a polished surface. In some specimens the kernel has a smooth integument, in others the kernel is covered by a thin layer of fibre. The proportion of fat in the kernels varies within wide limits according to the origin. In the following table I collate some recently published numbers obtained by several experimenters; to these are added three determinations made in the author's laboratory with nuts from authenticated sources.

[TABLE

Description.	Source.	Shells. Per cent.	Kernels. Per cent.	Percentage of Fat in Kernels.	Observer.
...	...	...	...	44	Schindler and Waschata [1]
...	West Africa	...	...	53·5	Drabble [2]
...	?	...	...	51·5	,,
Karité nuts .	?	...	...	34·0	,,
Shea butter nuts	Southern Nigeria (Oloke Meji Reserve)	29	71	35·96	Lewkowitsch [3]
,,	Northern Nigeria	58·9	41·1 [4]	47·82	,,
,,	Egyptian Soudan	32·5	67·5	44·0	,,
,,	Tengba (from Lagos)	...	...	54·4	Imperial Institute
,,	Bomo	...	...	48·0	,,
,,	Imported nuts	...	...	41·4	,,
,,	Kiln-dried nuts	...	...	46·2	,,

Older statements with regard to the yield of fat from the seeds refer to individual specimens only, and have, therefore, no general signification. Nor can the statement in older text-books that shea butter is characterised by a grey or greyish-white colour be maintained.

The fat is extracted by the natives by pounding the kernels and boiling the paste with water. The fat rises to the surface and is skimmed off into large calabashes, in which it is carried to the river, where traders collect it and take it down to the coast.

Little care being taken in the preparation, much of the shea butter that comes to Europe has a grey or whitish-grey colour and is characterised by a strong indiarubber-like odour and taste. More care is taken by the natives in the preparation of shea butter for their own purposes, only the freshest kernels being used. The fat so obtained is made up into cakes and wrapped round with leaves to protect it from becoming rancid. Preserved in this manner, the fat will keep fresh for several months. In proof of the statement that the grey colour must not be considered characteristic of shea butter, it may be mentioned that a number of shea butters extracted in the author's laboratory from different nuts furnished a pale yellow fat with not quite so pronounced an indiarubber-like taste as commercial samples possess. The fat expressed in this country from shea nuts is known as "shea nut oil." The press cake contains only 1·5 per cent of nitrogen; its high proportion of carbohydrates renders it useful for making "compound" cakes.

Pfaff's [5] statement that shea butter consists of tristearin and

[1] *Zeit. f. ang. Chem.* 1905, 305.

[2] *Quart. Journ. Inst. Comm. Research in the Tropics* (Liverpool University), 1906, i. 67.

[3] Unpublished determinations.

[4] In this case the nuts were still covered with the fibrous layer. The percentage of kernels calculated to the smooth nuts, freed from the fibrous layer, would be 51·4. The 58·9 per cent in the above table represent, therefore, shells and fibrous layers added together. The latter formed about 20 per cent of the total fruits.

[5] *Muspratt's Chemie*, 4th edition, vol. iii. p. 574.

triolein, in the proportion of seven parts of the former to three parts of the latter, is not borne out by the iodine values ascertained in the author's laboratory.

The author has, therefore, examined a number of different shea butters with a view to determine directly the percentage of stearic acid. This was found to vary from 33·7 per cent to 37·3 per cent.

According to the state of freshness of the fat the proportion of free fatty acids varies. The samples examined in the author's laboratory had acid values varying from 12·5 to 29. The saponification value also varies considerably in different specimens, as is shown by the numbers recorded in the table of characteristics under the heading "saponification value." This is due to the variation in the amount of unsaponifiable matter, which in the different specimens examined by the author was found to be from 3·6 to 9·7 per cent. The unsaponifiable matter seems to cause the indiarubber-like smell and taste. A process for the isolation of this substance (shea gutta ?) has been patented by *Rocca*, *Tassy* and *Roux*.[1]

The considerable amount of unsaponifiable matter in shea butter militates against its being used for soap-making purposes. Its indiarubber like taste would seem to preclude the hope of preparing an edible fat from shea-butter.[2]

Shea butter would seem to form a good raw material for candle-making, provided the fatty acids crystallise readily. *Kassler*[3] obtained, by hydrolysing shea butter in an autoclave under a pressure of 9 atmospheres with 3 per cent of magnesia, 92 per cent of fatty acids of the solidifying point 48·4° C. On distilling the fatty acids on a large scale, the samples taken from the condenser during the first twenty-four hours had solidifying points from 48·9° to 51·3° C., and iodine values from 47·03 to 51·32. In the following six hours of the distillation process small amounts of hydrocarbons were formed, increasing from 0·34 per cent to 5·07 per cent.

NJAVE OIL, NJAVE BUTTER, NARI OIL, NOUMGOU OIL

French—*Beurre de Njave (Djave); huile de Noumgou.*
German—*Njavebutter; Njariöl.* Italian—*Olio di Njave.*

This oil is obtained from the seeds of *Mimusops Njave* (Lanessan), Engler [Synonyms are:—*Bassia Djave*, De Lanessan; *Bassia toxisperma*, Raoul; *Tieghemella africana*, Pierre; *Baillonella toxisperma*, Pierre; *Baillonella Djave*, Pierre; *Tieghemella Jollyana*, Pierre], a

[1] French patent 364,368; German patent 191,736. Cp. also D. Spence, *Quart. Journ. Inst. Comm. Research in the Tropics* (Liverpool University), 1908, 61.

[2] At the Marseilles Colonial Exhibition of 1906 there was exhibited an edible fat stated to have been prepared from shea butter and having the melting point 38-39° C. The author was, however, not afforded an opportunity of tasting it.

[3] *Augsburger Seifensieder Zeitung*, 1902, 311.

tree[1] belonging to the family of the *Sapotaceæ*, which also includes *Bassia Parkii*, yielding the shea butter. The tree is indigenous to West Africa, Cameroons, Gaboon, Nigeria, and furnishes, like most trees belonging to the *Sapotaceæ*, gutta-percha (cp. "Surin Fat," below). In the Cameroons the tree is known to the natives as "Noumgou," and in Gaboon as "Njave" or "Djave." The fruits are termed by the natives "Ouréré." In the Gold Coast Colony the fruits are known as "Bako (Abeku) Nuts"[2] ("Mahogany Nuts").

The weight of the individual nuts varies between 10 and 15 grams, one-third of which is made up by the shell. The kernels contain 50 per cent of a white fat, which is solid at the ordinary temperature.[3] "Stearine" commences to separate at 31° C.; at 19° the whole mass is solid. The specimen of Njave butter examined by *Wedemeyer*[3] had undergone a considerable amount of hydrolysis, for it contained 19 per cent of free fatty acids; the amount of insoluble fatty acids + unsaponifiable was, therefore, somewhat high, viz. 96·1, of which 3·66 per cent formed the unsaponifiable matter. The specimen examined by *Freundlich*[4] had the acid value 13·8; and the amount of unsaponifiable matter was 2·20.

The following characteristics were determined by the observers named :—

	Wedemeyer.	Freundlich.
Specific gravity	0·8979 at 40° C.	0·9167 at 15° C. (water at 15° = 1)
Saponification value	185·3	182
Iodine value	56·1	56
Reichert-Meissl value	1·2	0·7
Maumené test	55° C.	...
Butyro-refractometer at 40° C.	52 "degrees"	...
Solidifying point of insoluble fatty acids	44·1° C.[5]	46[6]
Melting point (in capillary tube)	46·6° C.	...
Neutralisation value	201·7	...
Mean molec. weight of the fatty acids	...	284·6
Acetyl value (Lewkowitsch)	13·4	15·7[7]; 7·1[8]
Saponification value of acetylated fat	...	195·3

[1] *Les Végétaux utiles de l'Afrique tropicale française*, fascicule ii., par Em. Perrot. Paris, 1907.

[2] Catalogue of Exhibits of the Gold Coast Colony, Franco-British Exhibition, 1908.

[3] *Chem. Revue*, 1907, 35.

[4] *Chem. Revue*, 1908, 79; 106.

[5] The insoluble fatty acids included the unsaponifiable matter; at any rate no statement to the contrary has been made by the author.

[6] The insoluble fatty acids were free from unsaponifiable matter.

[7] Distillation process. [8] Filtration process.

AOUARA OIL—TUCUM OIL [1]

French—*Huile d'aouara, Huile de Tucum.*
German—*Aouaraöl, Tucumöl.* Italian—*Olio di aouara, Olio di tucum.*

This oil is obtained from the aouara palm, *Astrocaryum vulgare*, Martens, which occurs in French Guayana. In older text-books this oil is frequently described as a kind of palm oil. (The French colonists distinguish two kinds of oil palms: *Aouara d'Afrique*, or *A. de Guinée* (*Elœis guineensis*), and *Aouara de la Guayane* (*Astrocaryum vulgare*), and therefore the corresponding oils are known as Aouara oil of Guinea and Aouara oil of Guayana (Duchesne, *Catalogue des colon. françaises*, 1867, p. 88).

As in the case of the true African oil-palm, the fruits of the aouara palm grow in bunches. The fruits are oviform and have the size of a nut. They consist of a fleshy, fibrous pulp, in which is embedded the aouara oil, and of a very hard black nut (harder than the true palm nut) in which is enclosed a hard, irregular kernel.

The oil obtained from the kernel differs from that recovered from the fleshy part in the same manner as palm kernel oil differs from palm oil. The kernel oil will therefore be described separately (see below, under "Cocoa Nut Oil Group").

The fruits which were examined by *Bontoux* [2] were dry, although well preserved. Fifty fruits weighed 860 grams. They consisted of fibrous pulp, 24·2 per cent; shells, 50·4 per cent; kernels, 25·4 per cent. The fibrous pulp gave on extraction with petroleum ether 31 per cent of a golden-yellow [3] fluid fat, from which "stearine" separated on cooling. The acid value of this fat was 31·4. The following characteristics were ascertained by *Bontoux*:—

Specific gravity at 15° C.	0·916
Saponification value	196·5-197·2
Iodine value	74·8-75·7
Fatty acids + unsaponifiable	95·0 per cent.
Titer test of the fatty acids	32·2° C.
Neutralisation value of the fatty acids	198·5-199·7
Mean molecular weight ,,	281·0

The oil is prepared by the natives in the same manner as palm oil is obtained in West Africa. It serves for culinary purposes.

[1] Although this fat has a higher iodine value than the preceding fats, its close relationship to palm oil justifies its position here.

[2] Cp. Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires, traduit par E. Bontoux*, Paris, vol. ii. p. 1043.

[3] In the older literature the oil is stated to have a vermilion red colour, which persists, even on keeping the fat for years. It is also stated (Wiesner, *Die Rohstoffe des Pflanzenreichs*, 1900, vol. i. 488) that the colouring matter cannot be removed by boiling with water, but is "bleached" by heating the fat whilst it is exposed to the air; the colouring matter is also said to be destroyed by oxidising agents.

PALM OIL

French—*Huile de palme.* German—*Palmoel.*[1]
Italian—*Olio di palma.*

For tables of characteristics see pp. 443, 444.

Palm oil is obtained from the fleshy part of the fruit of the palm tree *Elœis guineensis*, L. (Jacq.), which form vast forests along the West Coast of Africa, extending between Gambia and St. Paul de Loanda. The West Coast of Africa is practically the only source of palm oil.

Another species of the palm tree, viz. *Elœis melanococca*, Gärt. (*Alfonsia oleifera*, Humb.), is cultivated in South America (Venezuela), in the province Amensis in Brazil, in the West Indies, in Java, and North Burmah. But the quantities obtained from this tree are very small; at any rate they do not reach the European market. The American palm is smaller than the African; its fruits are reddish. To this colour is due the local name "Coroza Colorado."

The favourite habitat of the palm tree is the open country or bushland, and it grows frequently where the natives have cleared the virgin forest. The tree is characteristic of the coast line and the lower reaches of the rivers. It will grow in all soils, but does not bear well at a higher elevation than 3000 feet. Under favourable conditions the tree forms a trunk when five years old, and lives for about fifty to sixty years. There are two main crops; in some regions four, or even five, are gathered in the year. The chief crop and the one yielding the better oil is that gathered in the early months of the year. Hence the best oil arrives in Europe after June. The heaviest shipments of palm oil come from the coast between May and August; those from the Gold Coast, Dahomey, and the Lagos districts are earlier than from Bonny, Opobo, Old Calabar, etc. (termed "river oils"). The second crop is gathered in October and November. The chief supply from the Niger district (Southern Nigeria) arrives in Europe from October to February.

Palm oil is obtained from the outside fleshy portion of the ripe fruit. Owing to climatic conditions, the process of extraction, which is practised exclusively by the natives, is an exceedingly crude one. When the fruits ripen, the men climb up the trees and cut off the bunches with "matchets."[2] Owing to the height from which the bunches fall, a large quantity of the fruit is bruised, which naturally leads to rapid fermentation and to hydrolysis of the oil. The women and children pick the fruit from the bunches and throw it into a hole dug in the ground and lined with leaves. The flesh of the fruit is at this time hard, and before the kernels can be separated the flesh must be softened. This is done by sprinkling water on

[1] In the German literature the name "palm oil" is given promiscuously to all fats derived from plants belonging to the palm family, so that not only palm nut oil but also cocoa nut oil is frequently referred to as palm oil. Such misnomers are apt to lead to confusion.

[2] This name is a corruption of the Spanish word "macheta," *i.e.* cutlass.

the fruit, covering it over with more leaves, weighted by stones and wood, and leaving for about two weeks. During this period fermentation sets in, which causes the fleshy part of the fruit to be softened, so that the kernel—palm nut—can be removed more readily. This is done by men, who place the fermented fruits in a mortar, roughly made by lining a hole made in the ground with large flat stones. The fruit is then beaten with long wooden pestles, or the pulp is pressed by hand. The beaten pulp together with the nuts is taken out by women and children and placed over another hole, the sides of which have been cemented by plastering with a mixture of palm oil and wood ashes. The pulpy mass is then allowed to rest for a week. During this time the oil drains into the cemented hole, from which it is ladled out into large calabashes of a size to make up one load.

The oil so prepared represents a superior kind of product. Women and children then pick out the nuts from the pulp, mix the pulp with water and place it in large iron cauldrons, where the whole mass is well boiled and stirred till the oil rises to the top. The oil is skimmed off, and in some regions mixed with the first extracted oil or put into separate vessels for the market. Finally, the residue is placed in a bag and squeezed over a hole so as to force out the liquid, from which more oil rises to the top. This oil contains a large quantity of water, and is again boiled out, skimmed off, and placed in calabashes.

The oil is carried—mostly by women—to the nearest coast or river station, where traders collect it in large barrels, and take it down to the coast station. There the oil frequently undergoes a rough purification by being boiled up with water, whereupon it is poured through sieves into barrels ready for shipment.

A special kind of oil is prepared by boiling the freshly picked fruit with water and preserving the skimmed-off oil for food purposes. This oil is prepared for each household, and is not exported. It is known as "Chop Oil."

It will readily be understood that this crude process, which is practised more or less in the same manner in all the African villages,[1] and seems to be a survival of the process by which olive oil has been produced in North Africa up to a few decades ago, is an extremely wasteful one; enormous quantities of oil are lost in consequence of this mode of extraction. It has been attempted to introduce portable machinery for the more economical working up of palm oil, and there are in the market several machines of this kind. One of these constructed by *Haake* (to which a prize was awarded by the Kolonialwirtschaftliche Komitee in Berlin) consists of a pulping machine and a hydraulic press. In the pulping machine the fruit is treated in the hot and the fleshy part is stripped off the nuts. The pulp is then expressed in the hydraulic press.

[1] For a description of the processes in vogue in Dahomey, cp. Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires, traduit par E. Bontoux*, Paris, vol. ii. p. 1046.

Owing to the fact that the recovery of palm oil is a kind of house industry, and to the distance of the villages from the river, there is very little prospect of machinery being introduced to a notable extent in the near future. Private information given to the author states that the working of *Haake's* machines has not been attended with success. A similar machine was patented recently by S. C. Phillips.[1]

In the above-described processes of preparing palm oil the seeds remain intact.[2]

To produce one ton of oil, 1400 bunches of fruit are required in the best managed districts. Besides the oil, about two tons of kernels are obtained. In the more remote villages where the work is carried on less carefully, up to 6000 bunches are stated to be required for one ton of oil.

The average weight of the fruit, as ascertained at the Botanic Gardens at Victoria (Cameroons), is 6·6 grams, of which the pulp forms 2·47 grams. The average weight of the kernels is 0·96 grams, whilst the shells of the seeds weigh on the average 3·17 grams. According to these figures, 100 grams of fruit would yield *fruit pulp* 37·5 per cent, *seeds* 62·5 per cent. The 37·5 per cent of pulp is made up of 32·8 per cent of palm oil, the remaining 4·7 per cent being water and waste fibre. The 62·5 per cent of seeds consists of 47·92 per cent of shells and 14·58 per cent of kernels, which latter contain about 50 per cent of fat (see p. 442). Careful experiments made with fruit of the average weight of 6·6 grams showed that whereas the natives require 1370 bunches for the production of one ton of oil, the same quantity of oil could be obtained from 405 bunches consisting of 1650 fruits each (exclusive of the kernels).

From these experiments it follows that the natives lose about two-thirds of the oil obtainable. Of course these last figures can only be taken as typical for the country from which the palm fruits have been taken, as the size of the fruit and yield varies considerably. Thus the pulp forms according to the variety of the palm tree, 27-70 per cent of the total fruit, whilst the kernels, freed from the shells, form 9-25 per cent. *Fendler*[3] recently examined four varieties of palm fruits, locally known under the names *De*, *De-de bakui*, *Se-de*, and *Afa-de*. The following are the results of his examination :—

The fleshy part of fruit contains—	1 De.	2 De-de bakui.	3 Se-de.	4 Afa-de.
	Per cent.	Per cent.	Per cent.	Per cent.
Oil	66·5	58·5	59 2	62·9
Moisture	5·3	5·7	6·9	5·6

[1] English patent 9733, 1906.

[2] A proposal to crush fruit and kernels together so as to obtain a mixed oil (pulp oil and kernel oil) has recently been patented by *A. Hallet*, French patent 321,918.

[3] *Berichte d. d. pharm. Gesellsch.* 1903 115.

Besides these four recognised varieties of palm trees, there exist in the Cameroons two other varieties, termed the small-fruited and large-fruited "Lisombe palm,"[1] which differ from the ordinary palm tree in that the shells enclosing the kernel are more brittle than those of the ordinary palm nuts. The following table gives some information as to the Lisombe varieties,[2] contrasted with the ordinary palm fruit :—

Variety.	Pulp in whole Fruit.	Palm Oil in whole Fruit.	Palm Oil contained in Pulp.	Kernel in whole Fruit.	Palm-kernel Oil in whole Fruit.	Oil contained in Kernel.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Small-fruited Lisombe .	71·0	32·66	46·0	9·54	4·91	49·2
Large-fruited Lisombe, ripe	71·0	44·44	62·5	12·5	6·15	48·9
Large-fruited Lisombe, unripe . . .	64·5	40·35	60·5	17·27	8·5	49·2
Ordinary Palm . .	37·5	22·64	60·3	14·58	7·13	48·9

In the Togo district (Misahöhe, German colony) there occurs besides the ordinary species called locally *E-de* and *De-ti*, also another species, called locally *Séddé*, which is poorer in oil, and is perhaps identical with the *Se-de* species described by *Fendler*. The fruits from the first kind are differentiated from the latter by their ovoid shape and bright red colour. Besides this species there also occurs another variety rich in oil — termed by the natives *Klu-dé*. This species, however, does not provide palm oil for export.

At the Gold Coast there occur four well-marked forms of oil-palms which are described by *Evans*[3] as follows :—

(1) *Abetuntum* or *Yue Yumu*, bearing black fruits which yield 13·77 per cent of oil.

(2) *Abepa* or *Yue*, the fruits of which yield 11·2 per cent of oil.

(3) *Abedam* or *Yue-hlem*, bearing reddish-yellow fruits which are larger than those of the other varieties. The fruits yield 11·2 per cent of oil.

(4) *Abobo-be* or *Yue Wyiam*, which represents the best variety on the Gold Coast. The shell of the kernel is much thinner than that of all the other varieties, and is so soft that it can be cracked with the teeth. (In this respect it resembles the Lisombe palm in the Cameroons.) The fruits are reddish-black, and yield 19·3 per cent of oil (see Appendix).

The fruits obtained from Benin and Calabar were found by *Drabble* to contain 24·8 and 29 per cent respectively of palm oil.

[1] Preuss, *Der Tropenpflanzer*. Cp. also Smend, *Der Tropenpflanzer*, xii. No. 6.

[2] According to Drabble (*Quart. Journ. Inst. Comm. Research in the Tropics*, 1908, 18), the Lisombe (Issombe) palm resembles the Abobo-be palm of the Gold Coast.

[3] *Quart. Journ. Inst. Comm. Research in the Tropics*, 1908, 18.

Physical and Chemical Characteristics of Palm Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9209-0·9245	Tate	38 [1]	Fendler	From 27 to 42·5		202-202·5	Valenta	53	Tolman and
18	0·946	Stilurell	39 [2]	,,	according to		196·3	Moore		Munson
50	0·8930	Allen	37 [3]	,,	age and origin		201-202	Thoerner	56	Lewkowitsch
(water 15·5=1)			31 [4]	,,	of the oil.		205·52 [1]	Fendler	53·38 [1]	Fendler
98-99	0·8586	,,			42 [1]	Fendler	203·78 [2]	,,	53·18 [2]	,,
(water 15·5=1)					43 [2]	,,	201·9 [3]	,,	57·44 [3]	,,
					41 [3]	,,	200·8 [4]	,,	55·68 [4]	,,
					35 [4]	,,				

Physical and Chemical Characteristics of Palm Oil—continued

Reichert-Meissl Value.		Refractive Index.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 60° C.	Observer.
0·86 [1]	Fendler	1·4510	Thoerner
0·74 [2]	,,		
1·87 [3]	,,		
0·90 [4]	,,		

[1] From De palm ; the oil contained 54·06 per cent free fatty acids (calculated to oleic).
[2] From De-de bakui palm ; ,, ,, 55·07 ,, ,, ,,
[3] From Se-de palm ; ,, ,, 55·38 ,, ,, ,,
[4] From Afa-de palm ; ,, ,, 57·18 ,, ,, ,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
95·6 94·2-97	Hehner Tate	98-99 (water 15·5=1) 100 (water 100=1)	0·8369 0·8701	Allen Archbutt	Average 44·13 As a rule 44·5-45; rarely 39-41 or 45·5-46·2 42·5-43 42·7 45·5 Highest 45·4-45·5 Lowest 35·8-35·9	De Schepper and Geitel Valenta Hübl Allen Lewkowitsch ,,	47·75 47·8 50	Valenta Hübl Allen	206·5-207·3 204	Valenta Thoerner	273 270	Tate Allen	53·3	Thoerner
													Liquid Fatty Acids.	
													94·6 99	Lewkowitsch Tolman and Munson

The following table [1] furnishes an instructive comparison of palm fruits from various districts :—

Ratio of	New Calabar.	Old Calabar.	Lagos.	Dixcove.	Warri.	Benin.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pericarp[2] to whole fruit	...	38·76	24·65	30·89	23·36	35·67
Pericarp fat ,, ,,	...	29·02	14·38	20·94	14·01	24·86
Pericarp fat to whole pericarp . . .	...	74·88	58·33	67·8	60·0	69·69
Kernel to kernel and shell . . .	20·4	22·81	25·0	31·06	23·17	20·17
Kernel oil to kernel and shell . . .	5·2	4·7	5·0	12·42	4·81	5·04
Kernel oil to kernel .	25·0	20·58	20·0	35·0	21·05	25·0
Average volume of fruit in c.c. . . .	...	7·2	4·0	5·2	6·7	7·5

The bulk of palm oil is shipped to Liverpool. Smaller quantities go to the north of Europe, Marseilles, and Hamburg. The following tables give detailed statistics as far as they are available :—

Imported to the United Kingdom

Year.	Tons.
1900	43,025
1901	51,161
1902	57,311
1903	53,252
1904	51,021
1905	45,941
1906	54,061
1907	60,743

Exported from the United Kingdom

Year.	Tons.
1900	31,219
1901	34,443
1902	39,041
1903	36,425
1904	35,920
1905	34,674
1906	33,771
1907	41,908

[1] E. Drabble, *Quart. Journ. Inst. Comm. Research in the Tropics*, 1907, ii. No. 5, 126.

[2] "Pericarp" denotes in this case the fleshy part of the fruit only, and not—as it should do in a strictly scientific sense—the stony shell of the kernels.

Imports of Palm Oil into France and Marseilles

In tons (of 1000 kilogrammes)

Year.	France.		Marseilles.
	Imports.	Exports.	Imports.
1896	16,227	525	8,803
1897	11,820	235	6,732
1898	15,675	239	7,182
1899	17,759	388	12,624
1900	22,345	324	15,912
1901	17,760	72	10,351
1902	20,592	419	11,161
1903	18,109	364	12,236
1904	16,317	442	11,972
1905	17,263	441	13,203
1906	14,333	163	8,631

It is impossible to give the imports into Germany, as the imports of palm oil are included in the statistical data for solid fats. It may, however, be stated that the value of the oil exported from Togo and Cameroon in 1906 was £350,000.

In the trade the oils are classified as follows :—

1. *Soft oils*, notably Lagos, Calabar, Opobo, Bonny.
2. *Hard oils*, Congo, Niger, Oil River, Liberia, Gold Coast.
3. *Mixed oils* from the Gold Coast and Niger district.

Statistical details as to the quantities exported from the individual districts of West Africa are now being collected more carefully. At present only the following details are available :—

Sierra Leone

Year.	Value.
1901	£9,816
1902	13,544
1903	14,068
1904	16,245
1905	18,524
1907 (615,997 gallons)	51,154

[TABLE

Gold Coast

Year.	Gallons.	Value.
1895	4,338,627	£231,415
1896	2,394,563	126,857
1897	2,021,716	107,737
1898	2,145,138	114,288
1899	3,323,919	183,204
1900	4,238,685	238,812
1901	3,146,390	178,171
1902	4,227,655	235,211
1903	2,589,591	145,896
1904	2,236,703	128,752
1905	1,598,272	88,359
1906	2,143,118	125,008
1907	1,867,945	119,468

Ivory Coast

Year.	Kilos.
1901	5,113,644
1902	6,173,007
1903	4,863,561
1904	5,839,970
1905	3,270,578

Lagos

Year.	Gallons.	Value.
1890	3,200,824	£190,657
1891	4,204,825	252,958
1892	2,458,260	137,743
1893	4,073,055	252,051
1894	3,393,533	187,928
1895	3,826,392	205,553
1896	3,154,333	159,150
1897	1,858,968	97,590
1898	1,889,939	97,337
1899	3,292,881	168,457
1900	2,977,926	190,165
1901	3,302,055	207,468
1903	...	218,245
1904	...	219,114
1905	...	179,006

Lagos is now included in Southern Nigeria. According to the latest statistical data the value of the palm oil exported by this colony was, in 1905, £868,028 (14,157,384 gallons); in 1906, £1,001,648 (16,032,571 gallons); and in 1907, £1,313,912 (18,332,531 gallons).[1]

[1] Earlier statistical data for Southern Nigeria, the Porto Novo transit lots included, are—

Year.	Gallons.	Value.
1900	12,741,585	£681,296
1901	15,894,404	813,478
1902	17,966,857	957,637
1903	15,192,135	847,954
1904	16,225,175	929,168

French Colonies

In tons (of 1000 kilogrammes)

Year.	Senegal.	French Guinea.	Ivory Coast.	Dahomey.	French Congo.
1900	...	61	4340	8,920	112
1901	...	199	5114	11,290	116
1902	...	182	6173	12,676	170
1903	...	94	4863	6,964	98
1904	9	171	5840	8,368	152
1905	12	23	3270	5,537	159
1906					

Palm oil has a somewhat sweetish taste; in its perfectly fresh state it is used as a culinary fat in the villages of the West Coast of Africa. Its odour is pleasant and resembles that of violets; this odour is not destroyed by bleaching with air at elevated temperatures, and persists even after the oil has been made into soap. In consequence of the very crude mode of producing palm oil, causing it to remain for a considerable time in contact with fermentable vegetable tissue, hydrolysis rapidly sets in, so that the oil on reaching the coast contains already a notable amount of free fatty acids. Palm oil when shipped from the coast has at least 10-12 per cent of free fatty acids. The process of hydrolysis, once begun, continues in the barrels during the voyage, and in consequence thereof commercial palm oils, on arriving at their destination, contain frequently from 20 to 50 per cent, and even more, of free fatty acids. In such palm oils free glycerol is found.[1] In old samples the hydrolysis may even reach completion, so that such palm oil practically consists of free fatty acids (*Lewkowitsch*). The progress of hydrolysis can be observed even in oils kept in glass bottles. Thus a sample of Drewin oil, which had originally the acid value 41·8, showed after six (summer) months the acid value 70·1.

The value of a palm oil in the markets depends on the care with which it has been prepared, as also on the particular locality from which it is derived. The "soft" oils are those containing a small quantity of free fatty acids, whereas the "hard" oils contain a large proportion of free fatty acids. The best "soft" oils come from Lagos and Dahomey. Next in quality are the River Oils ("medium" oils); whilst the lowest quality, the hardest oil, is represented by Congo oil.

The following table, due to *Y. de Schepper* and *Geitel*,[2] gives the proportion of water, impurities, neutral fat, and the solidifying points of the insoluble fatty acids of a number of commercial brands of palm oil :—

[1] Cp. Stenhouse, *Liebig's Annalen*, 36 (1840), 55.
[2] *Dingl. Polyt. Journ.* 245, 295.

Kind of Oil.	Water.	Impurities.	Solidifying Point of Fatty Acids.	Neutral Fat.
	Per cent.	Per cent.	°C.	Per cent.
Congo	0·78-0·95	0·35-0·7	45·90	16-23·0
Saltpond[1]	3·5-12·5	0·9-1·7	46·20	15-25
Addah	4·21	0·35	44·15	18·0
Appam	3·60	0·596	45·0	25·0
Winnebah	6·73	1·375	45·6	20·0
Fernando Po	2·68	0·85	45·90	28
Brass	3·05	2·00	45·1	35·5
New Calabar	3·82	0·86	45·0	40·0
Niger	3·0	0·70	45·0	40·0-47·0
Accra	2·2-5·3	0·60	44·0	53-76
Benin	2·03	0·20	45·0	59-74
Bonny	3·0-6·5	1·2-3·1	44·5	44·0-88·5
Gr. Bassa	2·4-13·1	0·6-3	44·6	41-70·0
Cameroons	1·8-2·5	0·2-0·7	44·6	67-83
Cape Labon	3·6-6·5	0·7-1·5	41·0	55-69
Cape Palmas	9·7	2·70	42·10	67
Half Jack-Jack	1·9-4·2	0·7-1·24	39-41·3	55-77·0
Lagos	0·5-1·3	0·3-0·6	45·0	58-68
Loando	1·5-3 0	1·0-1·9	44·5	68-76
Old Calabar	1·3-1·6	0·3-0·8	44·5	76-83
Gold Coast	1·98	0·50	41·0	69
Sherboro	2·6-7·0	0·3-1·2	42·0	60-74
Gaboon	2·0-2·8	0·3-0·7	44·5	79-93·0

The consistence of commercial palm oil varies from that of soft butter (Drewin[2]) to that of tallow (Congo oil). The colour also varies greatly, ranging, through all shades, from orange-yellow (Lagos) to dark dirty red (Congo).

The colouring matter of palm oil is not affected in the process of saponification by means of alkalis or lime; in the acid saponification process it is destroyed. It is also slowly destroyed by exposure to air, more rapidly on heating or by bleaching with chemicals. The two latter processes are adopted in practice for preparing bleached palm oil.

Since palm oil, as pointed out already, is bleached by mere exposure to the atmosphere, hydrogen peroxide contained in the atmosphere is assumed to be the bleaching agent. This finds support in the fact that *Schönbein* obtained with a specimen of palm oil the hydrogen peroxide reaction. This explanation has been further elaborated by *Engler*.[3]

Although palm oil can be bleached by means of ozone, yet several ozone processes examined by the author have hitherto not proved commercially successful, as the colour "reverts" in the palm oils so bleached. Bleaching by means of hot air, or by passing air through the heated oil, is capable of producing a tolerably white palm oil. The bleaching is carried out by blowing a current of air in a finely divided stream through the mass of oil, kept at a temperature

[1] This is the cheapest hard oil. [2] This is the cheapest soft oil.
[3] *Berichte*, 1900, 1101.

exceeding 100° C. According to the kind of palm oil, the temperature must be raised up to 150° C. Heating the oil to temperatures of 250° C. does not produce a better result. In these processes the characteristic odour of palm oil is not destroyed.

The bleaching process most in vogue, and that giving the best results, is the bichromate process. The oil is freed from its gross impurities, and treated according to its quality with 1-3 per cent of potassium bichromate and the requisite amount of hydrochloric acid. The dark "chrome" liquor is then carefully run off, and the oil is washed with water, at first with the assistance of a little mineral acid, until it is quite free from chromium and mineral acid.

Not all palm oils can be bleached successfully. Lagos and Old Calabar oils yield good results, but dirty-coloured red oils, such as Congo oil, have hitherto withstood all attempts to bleach them.

The chief constituents of palm oil are palmitin [1] and olein. The solid fatty acids consist, according to *Nördlinger*,[2] of 98 per cent of palmitic acid, 1 per cent of stearic, and 1 per cent of an acid described as a "heptadecylic" acid, $C_{17}H_{34}O_2$. This acid has, however, been shown by *Holde*[3] to represent a mixture in which an acid melting at 60-65° C., and of the mean molecular weight 288, could be identified. Two specimens of palm oil—Bassa raw, and Lagos bleached—examined in the author's laboratory yielded 0·53 per cent and 0·72 per cent of stearic acid respectively. *Hazura* and *Grüssner* found among the liquid fatty acids small quantities of linolic acid, identified by the sativic acid yielded on oxidation. This is confirmed by the iodine values of the liquid fatty acids recorded in the table (p. 444).

Colour reactions proposed for the identification of palm oil are useless, and in any case unnecessary, since palm oil cannot easily be confounded with other fats or oils.[4] It may, however, be stated that some specimens of palm oil—Lagos oil and Old Calabar oil—give with sulphuric acid a colour reaction similar to that obtained with cod liver oil in chloroformic solution, although the blue is much fainter; other specimens do not give this blue colour, but turn red at once.[5]

Palm oil is, as a rule, not adulterated with other fats, and its commercial valuation embraces, therefore, the determination of water, of impurities (mostly sand, added fraudulently by negroes), and of the solidifying point. The proportion of water and sand together should not exceed 2 per cent; for any excess, allowance is usually made by the seller.

[1] Palmitic acid was discovered in palm oil by Fremy, *Liebig's Annalen*, 36 (1840), 50.

[2] *Zeit. f. ang. Chemie*, 1892, 110. [3] *Berichte*, 1905, 1257.

[4] With regard to the detection of palm oil, when used as a colouring material for oils and fats, cp. Crampton and Simons, *Journ. Americ. Chem. Society*, 1905, 270. Small quantities (2-3 per cent) of palm oil used to be added to margarine ("oleomargarine") in the United States in order to give it a yellowish tint. As these colour tests appear to the author very uncertain, and, moreover, as the addition of palm oil to margarine is now forbidden by law, the reader must be referred to the original papers.

[5] Cp. Salkowski, *Zeit. f. analyt. Chem.* 1887 (xxvi.), 569.

Palm oil is chiefly used in the soap[1] and candle industries. In the latter industry it is valued *cæteris paribus* by its "titer." Being a non-drying oil, it is also employed in the tinplate industry, to preserve the surface of the heated iron sheet from oxidation until the moment of dipping into the bath of melted tin.

For the purposes of the tin industry "palm oil greases" are sold, consisting of palm oil adulterated with cotton seed oil and mineral oil of the spec. grav. 0·905.

GAMBOGE BUTTER

French—*Graisse (Beurre) de Gamboge.* German—*Gambogebutter.*
Italian—*Burro di Gamboga.*

Gamboge butter is the fat obtained from *Garcinia morella*, Desrouss., a tree common in the forests of Western India up to an altitude of 3500 feet; it is also frequently found in Ceylon. A variety of the fat, obtained from "Murga" seeds (*Garcinia*, sp. ?), is used for all cooking purposes like "ghee." A similar fat, from the seeds of the variety known as "Gurgi" (*Garcinia morella*), is used for lighting, cooking, and as a medicine for sprains and injuries (cp. also p. 489). The following characteristics are given by *D. Hooper*[2]:—

Fat

	Murga.	Gurgi.
Specific gravity at 50° C.	0·900	0·902
Melting point	37° C.	33·5° C.
Saponification value	198·20	194·74
Iodine value	53·72	55·46
Reichert-Meissl value	0·69	0·62
Acid value	3·49	13·79

Fatty Acids

Insoluble fatty acids + unsaponifiable	94·89 per cent	95·20 per cent
Melting point	56° C.	55° C.
Iodine value	56·38	57·81

The insoluble fatty acids of the "Murga" butter consist chiefly of stearic acid (about 30 per cent) and oleic acid; only small quantities of palmitic acid are present. *Hooper* conjectures that the fatty acids consist chiefly of dioleo-stearin.

[1] The negroes in the Togo district make a soap from palm oil and ashes obtained by burning banana leaves.

[2] D. Hooper, *Journal and Proceedings, Asiatic Society of Bengal* (New Series), vol. iii., No. 5, 1907, 258.

AKEE OIL [1]

French—*Huile d'Akée.* German—*Akeeöl.*
Italian—*Olio di akee.*

Akee oil is a yellow buttery fat, stated to be obtained from the arillus of *Blighia sapida*, Kon., a tree indigenous to tropical West Africa (Guinea Coast). Its cultivation was introduced into Jamaica between 1794 and 1838.

The fatty acids distil unchanged under a pressure of 13 mm. at 220°-225° C. They consist approximately of 50 per cent of oleic acid and 50 per cent of solid saturated acids. The acid value of the sample examined was 20·1.

The oil appears to be very similar to palm oil.

Physical and Chemical Characteristics of Akee Oil

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
99°-100° (water 15·5=1)	l° C.	° C.	Mgrms. KOH.	Per cent.	cc. $\frac{1}{10}$ norm. KOH.
0·857	20	25-35	194·6	49·1	0·9

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
Per cent.	99°-100° (water 15·5=1)	° C.	° C.	Mgrms. KOH.	Per cent.
93	0·8365	40-38	42-46	207·7	58·4
					Liquid Fatty Acids.
					82·4

[1] Garsed, *Pharmac. Journ.* 1900, 691.

MACASSAR OIL—KUSUM OIL

French—*Huile de Macassar.* German—*Macassaröl.*
Italian—*Olio di Macassar.*

For tables of characteristics see p. 454.

Macassar oil is the fat from the seeds of "Paka" ("pacca" in Calcutta), *Schleichera trijuga*, Willd. (the "Kusum"[1] tree of India, "Lac tree of Kosumba," "Ceylon Oak"), belonging to the *Sapindaceæ*.[2] The seeds consist of 40 per cent of shells and 60 per cent of kernels. The latter yield 70·5 per cent of a fat, which is known in India as "Kon oil," and in Celebes as "Ketjatkil oil."

According to a more recent examination, carried out by *J. H. Walker*, the kernels yield 60·4 per cent of oil, which is equivalent to 36·7 per cent of oil in the nuts examined.[3]

The fat forms at the ordinary temperature a yellowish-white buttery mass. It consists chiefly of the glycerides of lauric, palmitic, arachidic, and oleic acids, and contains also small quantities of acetic and butyric acids. The specimens examined by *Wijs*[4] yielded 45 per cent of solid and 55 per cent of liquid fatty acids. A very small proportion of hydrocyanic acid,[5] from 0·03 to 0·05 per cent (*Wijs*), seems to be characteristic of Macassar oil. A sample examined in the author's laboratory had the acid value 35·43. Specimens examined by other observers gave acid values varying from 6·2 to 19·2. The amount of unsaponifiable matter in the specimen examined by *Wijs* was 3·12 per cent.

In the Indian villages Macassar oil is employed as an illuminant, and the freshly expressed oil is used for cooking purposes in the United Provinces, and as a hair oil in the dangs of Bombay. The oil is also largely used for medicinal purposes, thus: as a purgative in the United Provinces, as a prophylactic against cholera in the Thana division of Bombay, and also externally in massage for rheumatism, for removing itch and other forms of skin diseases.

[1] This is the Hindustani name for the safflower plant, and perhaps refers to the colouring matter of the lac insect which often feeds upon the tree (D. Hooper, *Agricultural Ledger*, 1905, No. 1).

[2] The native name (in Celebes) of the seeds is Kusambi nuts; hence the alternative name *Cassambium spinosum*. Other botanical names of the plant are *Stadmannia sideroxylon*, Bl., and *Mellicocca trijuga*, Juss.

[3] *Agricultural Ledger*, 1905, No. 1.

[4] *Zeits. f. phys. Chemie*, xxxi. (Jubelband) 255.

[5] Probably liberated by the action of an enzyme on a cyanogenetic glucoside.

[TABLE

Physical and Chemical Characteristics of Macassar Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
0·924	Itallie	10	Glenk	22 22 [1]	Itallie Wijs	230 221·5 215·3	Itallie Lewkowitsch Wijs [2]	53 48·3 69·1 55	Itallie Lewkowitsch Roelofsen Wijs	9	Wijs

[1] By Crossley and Le Sueur's method.

[2] By *cold* saponification.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
91·4 91·5	Itallie Wijs	Titer Test. 51·6-53·2	Lewkowitsch	54-55	Itallie	191·2-192	Wijs	49·7-50·7	Lewkowitsch
								Liquid Fatty Acids.	
								103·2	Wijs

SAWARRI FAT [1]

French—*Huile de noix de Souari.* German—*Sawaributter.*
Italian—*Burro di noci di Souari.*

Sawarri fat is contained in the nuts from *Caryocar tomentosum*, Willd. (*Caryocar butyrosum*, Willd., *Caryocar nuciferum*),[2] imported occasionally from South America into this country as "butter nuts" from Demerara, where they are known under the name "Suari" or "Surahwa." The tree has been recently introduced into St. Vincent. The seeds contain 60 per cent of a fat which is colourless and possesses a pleasant, nutty taste. The free fatty acids in the specimen examined amounted to 2·4 per cent, calculated as oleic acid.

The solid fatty acids consist chiefly of palmitic acid. The liquid fatty acids contain besides oleic acid (identified by its oxidation product, dihydroxystearic acid) a hydroxylated acid which is readily converted into a lactone. The acetyl value of the liquid fatty acids was 14·03.

Physical and Chemical Characteristics of Sawarri Fat

Specific Gravity at 40° C. (water at 15° = 1)	Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert Value. c.c. $\frac{1}{10}$ norm. KOH.
0·8981	29-23·3	29·5-35·5	199·51	49·5	0·65

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value. Per cent.
96·91	47-46	48·3-50	272·8	51·5

MAFURA TALLOW [3]

French—*Suif (beurre) de Mafura ; graisse de Mafouraire.*
German—*Mafuratalg.* Italian—*Sego di Mafura.*

For tables of characteristics see p. 458.

Mafura tallow is contained in the seeds of (*Mafureira oleifera*) *Trichilia emetica*, Vahl. The fruits are small brown nuts, covered

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1890, 844 ; *Proceed. Chem. Soc.* 1889, 69.
[2] According to Semler, *Der Tropenpflanzer*, vol. ii. 449 (1887), the oil from this specimen of *Caryocar* is known as Pekeanut Oil.
[3] De Negri and Fabris, *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 271.

with a thin brown shell, which is easily detachable by rubbing; about 1600 nuts weigh one pound. The kernels amount to 88 per cent and the shells to 12 per cent of the whole nuts. On extracting the nuts with ether 61 per cent of fat is obtained, whilst the kernels alone yield 68 per cent, and the shells alone 14 per cent.[1]

The fat has a yellowish colour; it is free from taste. Its odour recalls that of cacao butter.

Suzzi[2] examined seeds from Ghinda (Erythrea, Italian East Africa). The seeds are about 18 mm. long and 8 to 12 mm. broad. The weight of 1 litre of seeds is about 520 grams. The kernels are white, but rapidly become brown on drying. The shells contain 51·2 per cent, the kernels 64·4 per cent, and the entire nuts 60·5 per cent of fat. *Suzzi* prepared separately the fat from the shells and that from the kernels. The examination gave the following results:—

	Fat from the Shells expressed in the Cold.	Fat from the Kernels expressed at 60° C.
Fat—		
Specific gravity	0·9192-0·9256 at 15° C.	0·857 at 100° C.
Solidifying point	4-3° C.	32-38° C.
Melting point	...	36-39° C.
Saponification value	203·6	198
Iodine value	65	44
Fatty Acids—		
Solidifying point	43-42° C.	50·5-48·5° C.
Melting point	46-47° C.	52-53·5° C.
Neutralisation value	201·2	205·8
Mean molecular weight	278·8	272·5

Two fats evidently corresponding to those examined by *Suzzi*, and prepared by the natives of Portuguese East Africa (where the fruits are known under the native names *Umkuhlu*, *Mkhuklu*, *Marba*, *Marwa-Maawa*, *Gnande*, *Mafoureira*, *Mafura*, or *Mafurrera*), were examined by *Daniel* and *M'Crae*.[3] The mode of preparation is not stated, beyond the indication that on boiling the fruits (with water?) a clear yellow oil—*mafura oil*—is skimmed off, which is used for cooking purposes, and that after the seeds are crushed *mafura tallow* is extracted. The latter is used by the natives for greasing the skin; it is considered by the natives to be poisonous, but the toxic properties have not been confirmed by *Daniel* and *M'Crae*. In the following table the results of *Daniel* and *M'Crae's* examination are collated:—

[1] *Bull. Imper. Inst.* 1903, 27.

[2] *I semi oleosi e gli oli*, published for the Milan Exhibition, 1906, 36.

[3] *Analyst*, 1908, 276.

[TABLE

	Mafura Oil.	Mafura Tallow.
Fat—		
Specific gravity at 15/15° C.	0·931	...
,, ,, at 30/15° C.	0·920	0·909
,, ,, at 40/15° C.	0·913	0·902
Melting point	...	29·5°-38° C.
Saponification value	202·5	201
Iodine value	66	43·5
Reichert-Wollny value	2·0	1·3
Saponification value of acetylated fat	235	218
True acetyl value	36·5	16
Butyro-refractometer; "degrees"		
,, ,, at 20° C.	65·6	...
,, ,, at 30° C.	60·1	...
,, ,, at 40° C.	64·6	47·3
Unsaponifiable	0·8 per cent	1·2 per cent
Free fatty acids	8·9 per cent	14·7 per cent
Insoluble Fatty Acids—		
Specific gravity at 92/15° C.	0·854	0·43
Solidifying point	44·2° C.	52·1° C.
Neutralisation value	201	204
Saponification value	206	205
Iodine value	68	46
Butyro-refractometer; "degrees"	37·2 at 50° C.	26·3 at 57° C.

"Mafura oil" does not give the *Halphen* test, and was found to be optically inactive.

Villon's statement that it consists of 55 parts of olein and 45 parts of palmitin requires confirmation. The high melting point of the insoluble fatty acids would seem to render this fat especially suitable for the manufacture of soaps and candles.

[TABLE

Physical and Chemical Characteristics of Mafura Tallow

	Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
I. Prepared in the Laboratory .	33-25	De Negri and Fabris	35-41	De Negri and Fabris	200·08	De Negri and Fabris	44·85	De Negri and Fabris
,, from the entire nuts	30-25	Suzzi	35-40	Suzzi	200·2	Suzzi	47·5	Suzzi
II. Commercial	37-30	De Negri and Fabris	35·5-42	De Negri and Fabris	220·96	De Negri and Fabris	46·14	De Negri and Fabris

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Solidifying Point.		Melting Point.		Neutralisation Value.		Saponification Value.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
I.	47-44	De Negri and Fabris	51-54	De Negri and Fabris	...	...	...	...	46·92	De Negri and Fabris
	49-46	Suzzi	51-54	Suzzi	194·3	Suzzi	197	Suzzi		
	49·5 (Titer test)	,,								
II.	48-44	De Negri and Fabris	52-55	De Negri and Fabris	...	...	...	...	48·19	De Negri and Fabris

Myristica Group

The members of this group belong to the family of *Myristicaceæ*, and are characterised by a large proportion of myristin. Some of these fats, like ochoco fat, consist almost entirely of myristin. The following fats—arranged, as far as is possible at present, in the order of their iodine values—are included in this group:—

(*a*) Nutmeg butter, Mace butter.
(*b*) Virola fat.
(*c*) Papua nutmeg butter.
(*d*) Otoba fat, Otoba wax.
(*e*) Fat from Virola Sebifera.
(*f*) Ocuba fat, Ocuba wax.
(*g*) Fat from Virola Micheli.
(*h*) Fat from Staudtia Kamerunensis.
(*i*) Kombo butter.
(*k*) Ucuhuba fat, Urucaba fat.
(*l*) Fat from Myristica Surinamensis.
(*m*) Ochoco fat.

Iriya oil,[1] the oil obtained from *Myristica iriya*, an evergreen shrub indigenous to Ceylon, appears to be an ethereal oil, as it is obtained from the bark. This oil was exhibited at the Paris Exhibition of 1900, and is stated to be applied by the natives as a remedy in cutaneous diseases.

(*a*) NUTMEG BUTTER, MACE BUTTER

French—*Beurre de muscade.* German—*Muskatbutter.*
Italian—*Burro di noce moscata.*

For tables of characteristics see pp. 463, 464. (See Appendix.)

Nutmeg butter is obtained from the seeds of *Myristica officinalis*, L. (s. *moschata*, Thunb., s. *fragrans*, Houtt.), a tree growing wild on the islands of the Indian Archipelago, notably Celebes, Sumatra, Java, Molucca, and the Banda Islands. The tree is now cultivated in these islands. By far the largest quantity of nutmegs imported into Europe comes from the Banda Islands. The tree is also cultivated in the West Indies, Brazil, and Guiana. The pericarp of the seed yields the arillus (mace) which is used in pharmacy, as a condiment for culinary purposes, and for the preparation of the ethereal oil contained in it. Formerly the small, as also the worm-eaten, rejected nuts which could not be exported were worked up for mace butter

[1] *Imperial Institute Journal* 1901.

on the islands of the Indian Archipelago. The nuts were ground to a coarse meal, filled into sacks, and steamed for about six hours over boiling-pots. The sacks were then placed in a strong press and subjected to pressure. The butter so obtained represented a brownish mass. This was exported in the shape of bars (resembling soap bars) wrapped in cocoa nut tree leaves (hence these bars were termed "soap of Banda"). At present mace butter is chiefly obtained in European works (Holland), where the nuts are powdered and expressed in the hot. The fat is also prepared in small quantities by extraction with petroleum ether,[1] or common ether, in pharmaceutical laboratories.

The world's annual production of nutmegs does not exceed 1500 tons. Only a small quantity thereof is used in the manufacture of nutmeg butter, so that the price of the fat is somewhat high. The seeds contain 38-40 per cent of fat. Nutmeg butter has the consistence of soft tallow, is of a yellowish colour, and has the strong taste and odour of nutmegs.

The commercial fat varies considerably in composition (see table below). It contains from 4 to 10 per cent of an ethereal oil[2] (hence the low saponification value), and consists of about 45 per cent of a solid fat, chiefly trimyristin; the rest being a liquid fat and free fatty acids.

Cold alcohol dissolves the liquid fat, the free acids, and the ethereal oil (unsaponifiable), leaving about 45 per cent undissolved. The undissolved portion yields on crystallisation from ether, pure trimyristin, melting at 55° C.

Boiling alcohol dissolves nutmeg butter almost completely. The solubility in alcohol is not only due to the high percentage of free fatty acids contained in the commercial samples, but also to the ready solubility of myristin itself in alcohol.

The following table contains a few characteristics ascertained by *Dieterich*; the first five samples were prepared by extracting nutmegs with ether :—

[1] The seeds contain 38 to 40 per cent of fat, but the yield obtained by expression hardly reaches 30 per cent.

[2] An exhaustive examination of the ethereal oil has been made by F. B. Power and A. H. Salway, *Journ. Chem. Soc.* 1907, 2037.

[TABLE

No. of Sample.	Specific Gravity at 15° C.	Melting Point. °C.	Acid Value.	Saponification Value.	Iodine Value.	Solubility in Parts of Boiling Alcohol.
1	...	...	22·4	156·8	...	...
2	...	...	22·4	159·6	...	...
3	0·996	51	22·4	154·0	...	15
4	...	...	22·4	156·8	...	...
5	...	...	22·4	156·8	...	...
6	0·945	42	39·2	151·2	...	12
7	0·957	45	33·6	140·0	...	12
8	0·966	48	44·8	134·0	...	10
9	...	38·5-39	17·25	178·25	45·32	...
10	...	42	19·60	173·13	42·71	...
11	...	43	18·67	172·2	40·14	...
12	...	42·5-43	18·67	174·54	41·38	...
13	...	39	21·93	175·93	52·04	...
14	...	38·5-39	22·80	178·67	48·60	...

The following are the results of an examination of commercial samples of nutmeg butter by *Spaeth* :—

Origin.	Melting Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer at 40° C. "Degrees."
Banda . .	25-26	170-173	77·8-80·8	4·1-4·2	76-82
Bombay [1] .	31-31·5	189·4-191·4	50·4-53·5	1-1·1	48-49 [1]
Menado . .	25·5	169·1	76·9-77·3	...	74-74·5
Penang . .	26	171·8-172·4	75·6-76·1	...	84·5-85
Macassar .	25-25·5	171·8-172·4	75·6-76·1	...	78·5
Zanzibar .	25·5-26	169·9-170·5	76·2-77	...	77·5

The discrepancies in the iodine values suggest the explanation that they may be caused by varying quantities of ethereal oil. An experiment carried out in the author's laboratory seemed, however, not to confirm this view, as a sample of genuine nutmeg butter of the iodine value 59·3 showed, after being freed from its ethereal oil by a current of steam, the iodine value 58·3.

From recent experiments made by *Fabris* and *Settimj* [2] it would appear that either the essential oil had not been driven off completely in this experiment, or that there are present in crude nutmeg butter other foreign substances which are not readily volatilised. *Fabris* and *Settimj* digested crude nutmeg butter *obtained by extraction with ether* with 95 per cent alcohol at a low temperature (not exceeding 5° C.), and thus resolved the crude nutmeg butter (the

[1] This fat is derived from *Myristica malabarica*, Lam. (see Appendix), and should therefore not have been included by *Spaeth* in the above-given table. (Private communication to the author from D. Hooper, Indian Museum, Calcutta.)

[2] *Atti del VI. Congresso internaz. di chemica applicata*, Roma, 1907, v. 756.

characteristics of which are given in the tables, p. 463) into an alcohol-insoluble, almost white and inodorous fat, and an oily, reddish-brown fat having a very pronounced smell of mace. The latter portion formed about 6 per cent of the crude fat. Some characteristics of the alcohol-insoluble and alcohol-soluble portions were ascertained by *Fabris* and *Settimj*; it would appear that the alcohol-insoluble portion is practically pure myristin (see Appendix).

	Fat insoluble in Alcohol at 5° C.	Oil soluble in Alcohol at 5° C.
Melting point	55 to 56° C.	...
Saponification value	226·1	46·8
Iodine value	7·0	114·3
Butyro-refractometer; "degrees" . .	35 at 50° C.	93·5 at 90° C.

Nutmeg butter is frequently substituted by fats from other species of *Myristica*. Recently the demand for mace butter has caused the importation of nuts from *Myristica argentea*, Warb., the so-called Papua nutmeg, growing wild in Dutch New Guinea (see below). It has been stated that commercial mace butter is frequently nothing else but Papua nutmeg butter (see (*c*)).

Adulteration with waxes or unsaponifiable (mineral) waxes can be easily detected.

In the East nutmeg butter serves for medicinal purposes.[1] In Europe the butter is official as *Oleum myristicæ*; it is used as a basis for ointments, etc.

[1] Krasser, *Chem. Revue*, 1897, 331.

Physical and Chemical Characteristics of Nutmeg Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.
15	0·945-0·996	Dieterich	41-42	Rüdorff	47-48	Rüdorff	154-159·6	Dieterich
15	0·9598	Fabris and Settimj	Turbid at 33	Wimmel	43·5-44	Wimmel	153·53-161	,,
					51	Dieterich	169·1-191·4	Spaeth
100	0·8840	,,	rising to		42	,,		
98-99	0·898	Allen	41·5-44		45	,,		
(water 15·5 = 1)					48	,,		
					38·5-43	,,		
			39-40	F. and S.	49-50	F. and S.		

Physical and Chemical Characteristics of Nutmeg Butter—continued

Iodine Value.		Reichert-Meissl Value.		Refractive Index.			Maumené Test.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	$(n)_D$ at 40° C.		Observer.	° C.	Observer.
40·1-52·0	Dieterich	1-4·2	Spaeth	1·4704		Utz	39	F. and S.
59·3	Lewkowitsch	2·1	F. and S.					
50·4-80·8	Spaeth			Butyro-refractometer.				
48·8-65·1[1]	Wijs							
50·1-85·7[2]	,,				"Degrees."	Observer.		
				At 40° C.	67·0	Utz		
				,,	61	F. and S.		
				At 50° C.	55	,,		

[1] Oils expressed in Europe.

[2] Indian oils.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
82·5 (?)	F. and S.	40 44-45	Hübl F. and S.	42·5 48-49	Hübl F. and S.	31·6	F. and S.
		Titer Test.				Liquid Fatty Acids.	
		35·5- 35·95	Lewko- witsch			93·5	F. and S.

(*b*) VIROLA FAT

The seeds of *Virola fat*, from *Virola venezuelensis*, Warb., known in Venezuela by the local name "cuajo," contain, like the seeds from *Myristica moschata*, besides the fatty oil, an ethereal oil. The seeds yield 47·5 per cent of a brown fat, from which pure myristin of the melting point 54°-55° C. can be obtained by crystallising twice from ether (cp. Vol. I. Chap. I.).

(*c*) PAPUA NUTMEG BUTTER

French—*Beurre de muscade de Papua.*

"Papua nutmeg butter," the fat from *Myristica argentea*, Warb., contains no ethereal oil, but is said to have the same characteristics as the fat from *Myristica officinalis* (see above).

(*d*) OTOBA FAT

Otoba fat, commercially known also as otoba wax, is the fat from *Myristica otoba*, Humb. and Bonp.

The otoba fat, which is known as American mace butter, is obtained in New Granada by pressing the seeds. In its fresh state it has a pleasant aromatic odour, like mace butter, but in the melted state it has an unpleasant smell. According to *Uricoechea*[1] the fat consists of myristin, olein, and a substance termed by him *otobit*. This substance is stated to crystallise in large prisms of melting point 133° C. (sitosterol ?).

[1] *Liebig's Annal.* 91, 369.

(*e*) FAT FROM VIROLA SEBIFERA

This fat is obtained by boiling the fruit from *Virola sebifera*, Aubl., with water. It forms a yellowish tallow-like mass, of slight ethereal odour, having the specific gravity 0·995 at 15° C., and melting at 45° C. The fat is stated to consist chiefly of myristin and olein, and is used commercially in Guiana in the manufacture of soaps and candles.

(*f*) OCUBA FAT

The fat from *Myristica ocuba*, Humb. and Bonp., commercially known as ocuba wax, is obtained from the fruits of a shrub similar to our hazel nut trees. The nuts are surrounded by a thick skin, which yields on extraction with water a pink colouring matter—ocuba red. The seeds yield 20-22 per cent of "ocuba wax."

This fat is a commercial article in Belem, the capital of the province Para in Brazil, and is used there as a candle-making material. An exhaustive examination of this fat has not been made yet. The specific gravity is stated by some writers as 0·920 at 15° C., and its melting point is given as 39°-40° C. These data render it extremely unlikely that "ocuba wax" is, chemically speaking, a wax; hence it is classed by the author amongst fats.

(*g*) FAT FROM VIROLA MICHELI

This fat is obtained from the nuts of *Virola Micheli*, Heckel,[1] a tree occurring in French Guiana. The arillus yields by extraction with carbon bisulphide 47·1 per cent of a mixture of ethereal oil and fat. The endosperm gave 65·41 per cent (51·25 per cent of the total seed) of a solid white fat which must have contained considerable quantities of foreign substances, including ethereal oil, as the specific gravity is stated by *Heckel* to be 1·043 at 15° C.

(*h*) FAT FROM STAUDTIA KAMERUNENSIS

The seeds of *Staudtia Kamerunensis*, Warb.,[2] freed from the arillus yield 31·7 per cent of solid fat of a yellow colour, and an aromatic taste and odour. The insoluble fatty acids solidify at 39·2° C., and are stated to consist of myristic and oleic acids.

[1] Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, p. 118.

[2] *Ibid.* p. 111.

(*i*) KOMBO FAT, KOMBO BUTTER

French—*Beurre de Kombo ; beurre de Mutage.*

This fat is obtained from the seeds of *Myristica angolensis*, Welw., which are known in the Jebu-Ode district of Southern Nigeria by the name "Acoomoo."[1] In the Gold Coast Colony the seeds are known under the native name "Ote seeds."[2] In the Gaboon this oil is known as *beurre de Kombo*,[3] in Angola as *beurre de Mutage* or *beurre d'Ikoum* (Panouin). The seeds are described by *Warburg* as being obtained from *Pycnanthus Kombo* (Baillon.), Warb. This latter tree is widely distributed in the Gaboon (where it is known as *arbre à suif du Gabon*), in the Congo, and Angola. The seed, after being freed from the arillus, but still retaining the shell, gave by extraction with carbon bisulphide 45·5 per cent of fat; the endosperm alone yields 56 per cent of a fat melting at 51° C., and solidifying at 49° C. The fat has a pleasant aromatic smell, but on standing is said to develop the odour of trimethylamine.

(*k*) UCUHUBA FAT, URUCABA FAT

French—*Graisse d'Ucuhuba.* German—*Ucuhubafett, Urucabafett.*
Italian—*Sego di Ucuhuba.*

For tables of characteristics see p. 467.

Ucuhuba fat is obtained from the nuts of *Virola bicuhyba*, Humb. It is stated that the fat from *Virola bicuhyba* is usually mixed in Brazil with that of *Myristica officinalis.* Owing to the crude method employed in its preparation, the fat as brought into the market is yellowish brown, and has an aromatic odour (due to a small quantity of an ethereal oil), recalling that of cacao.

Ucuhuba fat consists of myristin and olein (10·5 per cent), small quantities of an ethereal oil, of a resinous substance, and of a wax-like compound. The resinous substance resembles Peru balsam in odour; it is soluble in ether, hot alcohol, petroleum ether, and chloroform.

The sample examined by *Valenta* contained 8·8 per cent of free fatty acids.

[1] E. Drabble, *Quart. Journ. Inst. of Comm. Research in the Tropics* (Liverpool University), vol. ii. 1907, No. 5, 132.

[2] Catalogue of Exhibits of the Gold Coast Colony, Franco-British Exhibition, 1908.

[3] Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, p. 105.

Physical and Chemical Characteristics of Ucuhuba Fat

Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
...	...	39	Valenta [1]	219-220	Valenta	9·5	Valenta
32-32·5	Nördlinger	42·5-43	Nördlinger [2]				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.	
Per cent.	Observer.	° C.	Observer.
93·4	Valenta	46	Valenta
		42·5-43	Nördlinger

[1] *Journ. Soc. Chem. Ind.* 1889, 202.

[2] *Berichte*, 1888, 2617.

(*l*) FAT FROM MYRISTICA SURINAMENSIS

This fat is obtained from the "oil nuts," the seeds of *Myristica surinamensis*, *Virola surinamensis*, Warb. It has a crystalline structure, melts at 45° C. (*Reimer* and *Will.*),[1] and appears to have a chemical composition similar to that of ucuhuba fat. A specimen of crude commercial fat contained 87 per cent of triglycerides, 6·5 per cent of free myristic acid, and a caoutchouc-like (resinous) substance. To the presence of the last-named substance must be ascribed the fact that the crude fat is not completely soluble in petroleum ether or in boiling alcohol. The amount of insoluble fatty acids + unsaponifiable found by *Valenta* as 93·4 per cent includes, of course, the resinous substance.

(*m*) OCHOCO FAT[2]

French—*Beurre d'Ochoco.*

Ochoco fat is contained in the seeds of *Scyphocephalium ochocoa*, War., a tree indigenous to the West Coast of Africa. From a description published by *Pierre*[3] it appears that the nuts have no arillus and that they are non-dehiscent. He therefore looked upon the plant as representing a new genus of Myristicaceæ, and named the tree *Ochocoa gabonii*. Warburg,[4] in 1895, described the tree as *Scyphocephalium chrysothrix*, and later in 1897 as *Scyphocephalium ochocoa*.[5] The statement he made in 1895, viz., that the nuts had an arillus and are dehiscent, was corrected later on,[5] in so far that the question as to whether the nuts were possessed of an arillus or not was left open. A very large number of nuts examined some years ago by *Heckel*,[6] as also those submitted to the author, showed no sign of an arillus and hence would not yield ethereal oil.

The specimens examined by the author were identified by the Kew authorities as the kernels of *Scyphocephalium ochocoa*. The average weight of the kernels is 10 grams; the smallest weighing 5 grams and the largest 12·5 grams. The kernels together with the thin husks surrounding the endocarp yield 58·8 per cent of fat. By whatever process the fat is prepared, a dark brown colouring matter is at the same time extracted, which is so tenaciously retained by the fat, that the author has hitherto been unable to remove this colouring matter. Similar difficulties were met with by *Heckel* and his collaborators. This dark colouring matter is not only contained in the husks but also in the membranous extension of the husk (spermoderm) which passes through the whole of the endosperm, in the form of irregular lamellæ radiating from the *chalaza*. As the

[1] *Berichte*, 1888, 2011. [2] Lewkowitsch, *Analyst*, 1908, 313.

[3] *Bulletin de la Société linnéenne de Paris*, 1898, No. 5. *Séance du premier mai*, 1896.

[4] "Identificierung der sogenannten Ochoconüsse aus Gabun mit Scyphocephalium einer neuen Muskatnuss-Gattung," *Notizblatt des Königlich Bot. Gart.*, Berlin, 1895.

[5] Warburg, "Monographie der Myristicaceen, *Acta Leopoldina*, Halle, a/S lxviii. 1897.

[6] *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, 1902.

examination of the dark fat offered some difficulties, the only way to obtain a fat free from colouring matter was to cut out the white endosperm carefully by hand. The amount of endosperm so obtained formed 84·7 per cent of the kernels. These 84·7 per cent contained 69·4 per cent of fat.

The white endosperm, on being extracted in the usual manner, yielded a perfectly white fat of the acid value 1·42, which gave the following characteristics :—

Fat

Specific gravity at 60° C. (water at 4° = 1)	0·8899
Saponification value	238·5
Iodine value	1·72
Reichert-Meissl value	0·65
Insoluble volatile acids required	4·00 c.c. decinorm. KOH.
Melting point	45-48° C.
Unsaponifiable matter	0·37 per cent.

Fatty Acids

Mean molecular weight of the fatty acids, freed from unsaponifiable matter	221·9
Melting point (capillary tube)	47·2° C.
Iodine value	1·47

These numbers lie so near to those yielded by myristin that the fat may be considered as consisting of practically pure myristin, or about 98 per cent of myristin and about 2 per cent of olein. The mixed fatty acids gave on separation by means of the lead-salt-ether method 12·82 per cent of acids, the lead salts of which were dissolved by ether. The acids obtained from these lead salts were, however, solid : melted at 31·7-32·2° C. (in a capillary tube), and absorbed no more than 9·9 per cent of iodine.

The mean molecular weight of the insoluble volatile acids was found to be 227·3 (myristic acid = 228) ; they melted at 43·3-48·9° C. The mixed fatty acids lost by washing with a considerable quantity of boiling water were only 1·5 per cent. This shows that the acids consist practically of pure myristic acid, and inferentially that ochoco fat is free from laurin.

The natives apply the name " Ochoco " indiscriminately to several edible fruits, such as the fruits from *Lophira alata* (see " Niam Fat "), etc.

PHULWARA BUTTER, INDIAN BUTTER, GHÉ BUTTER, GHEE BUTTER, GHEE

French—*Beurre de Fulware* (*Ghé*, *Ghee*). German—*Fulwabutter*, *Phulwarabutter*. Italian—*Burro di Fulwara ; burro di ghee.*

For table of characteristics see p. 470.

This fat is expressed from the seeds of *Bassia* (*Illipé*) *butyracea*, Roxb., the Indian " butter tree " indigenous to the Himalayas. It

must not be confounded with Mowrah seed oil nor Mahua butter. The seeds contain 50-52 per cent of fat, which has the consistence of lard, and is stated to keep well, even in India, without becoming rancid.

The specimen examined by *Crossley* and *Le Sueur* had the acid value 16·44.

Phulwara butter is one of the most important food-stuffs amongst the natives of the North-West Provinces, on account of its pleasant odour and agreeable taste. The butter is also highly valued as an ointment, when properly perfumed; it is frequently adulterated in India with kokum butter and mahua butter.

Physical and Chemical Characteristics of Phulwara Butter

Specific Gravity at 100° C. (water 100° = 1)	Melting Point.	Saponific. Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable.	Refractive Index at 40° C.	Viscosity Seconds at 140° F.
	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refractometer. "Degrees."	
0·8970	39	190·8	42·12	0·44	94·86	48·2	110·4

SURIN FAT[1]

French—*Huile de Surin.* German—*Surinfett.*
Italian—*Sego di Surin.*

Surin fat is probably derived from the seeds of a species of *Palaquium.* It was obtained by the author from the Imperial Institute, and was described as "Minyak surin, from Perak, Straits Settlement." After removing some impurities by filtering, the following characteristics were ascertained in the sample containing 43·2 per cent of free fatty acids :—

Fat

Specific gravity at 60° C. (water at 60° C. = 1)	0·9021
Solidifying point, commences to solidify at	48·9° C.
,, ,, solid at	43·90° C.
Melting point (capillary tube)	56·1° C.
Saponification value	179·5
Unsaponifiable matter	4·54 per cent.
Iodine value	42·31
Reichert-Wollny value	0·55

Fatty Acids

Solidifying point	59·1° C.
Mean molecular weight	284·9
Stearic acid (of melting point 67·8° C.)	58·2 per cent.

[1] Lewkowitsch, *Analyst*, 1906, 2.

Evidently the fatty acids consist of a mixture of stearic acid and oleic acid only. The extremely high proportion of stearic acid would seem to render this fat a very useful raw material for the candle industry, although the considerable amount of unsaponifiable matter might militate against its use. (Possibly the high proportion of unsaponifiable matter is due to careless preparation of the fat.)

Although a number of species (eighteen) of the genus *Palaquium* (family of *Sapotaceæ*), all of which yield gutta-percha, have been described, the fats obtainable from them are hardly known. The seeds of *Palaquium pisang*, Burck (Sumatra), are stated to yield 45 per cent of a bitter yellowish fat, known in commerce under the name "Balam tallow."

From the seeds of *Palaquium oleosum*, Blanco (Sumatra), a white sweetish fat ("Suntei tallow") is expressed. *Palaquium oblongifolium*, Burck (Borneo), is said to yield a hard white fat ("Njatuo tallow") consisting chiefly of "stearine" (whatever this may mean). It is used in West Borneo as an edible fat. Recently *De Jongh* and *Tromp de Haas*[1] described the fat from *Palaquium oblongifolium*, Burck (which yields the best kind of gutta-percha), and gave the following figures :—

Yield of fat from seeds	32·5 per cent.
Melting point of fat	40° C.
Saponification value	201·5
Iodine value	34·3

The specimen examined by them was comparatively fresh, as the percentage of free fatty acid was only 2·1. It is stated to consist of 57·5 per cent of stearin, 36 per cent of olein, and 6·5 per cent of palmitin.

Obviously "Surin fat" does not differ much from the fat of *Palaquium oblongifolium*.

MKÁNYI FAT

French—*Suif de Mkany.* German—*Mkányifett.*
Italian—*Sego di Mkany.*

For tables of characteristics see p. 472.

This fat forms about 67 per cent of the seeds of *Stearodendron Stuhlmannii*, Engl. (*Allanblackia Stuhlmannii*, Engl.), an East African *Guttifera* (called Mkányi by the natives of Uluguru).

The fat, as prepared by the natives and marketed at Bogamoyo, is of yellowish-white colour. The acid values of various specimens of the native product were 23·33 (*Heise*); 11·6-20·7 (*Henriques*). According to *Heise*,[2] who first examined this fat, Mkányi fat consists chiefly of the mixed glyceride, oleodistearin (Chap. I.). No palmitic acid was found in the fat.

[1] *Chem. Rev.* 1904, 285.
[2] Heise, *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1896, 540.

Physical and Chemical Characteristics of Mkányi Fat

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9298	Henriques and Künne	38 at 39 crystals appear; remains liquid to 29·5, rising on solidifying to 36°.	Heise Henriques	40-41 completely melted at 42.	Heise Henriques	190·5 186·6-191·7	Heise Henriques	41·9	Heise	1·21	Heise
40	0·8926	Heise										
98 (water 15°=1)	0·85606	,,										
100	0·8606	Henriques										

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
95·65	Heise	57·5	Heise	59	Heise	42·1	Henriques
		61·4-61·6 (Titer test)	Henriques	61·5	Henriques		

RAMBUTAN TALLOW [1]

French—*Suif de Rambutan.* German—*Rambutantalg.*
Italian—*Sego di Rambutan.*

Rambutan tallow is obtained from the seeds of *Nephelium lappaceum*, L., indigenous to China and the Sunda Islands. The seeds contain 40-48 per cent of fat.

Physical and Chemical Characteristics of Rambutan Tallow

Specific Gravity.	Solidifying Point.	Melting Point.	Saponific. Value.	Iodine Value.
	° C.	° C.		
0·9236	38-39	42-46	193·8	39·4

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
° C.	° C.			
57	58-61	186·4	300·9	41·0

The high mean molecular weight of the insoluble fatty acids indicates the presence of fatty acids higher than stearic acid; indeed, arachidic acid was isolated, as also a small quantity of stearic acid; palmitic acid is stated to be absent. The proportion of oleic acid in the insoluble fatty acids was found to be 45·5 per cent.

MALABAR TALLOW, PINEY TALLOW,[2] WHITE DAMMAR OF SOUTH INDIA

French—*Suif de Piney (Malabar).* German—*Malabartalg, Vateriafett, Pineytalg, Pflanzentalg.* Italian—*Sego di Piney.*

For tables of characteristics see p. 474.

This fat is obtained from the seeds of *Vateria indica*, L., a tree indigenous to the East Indies. The fat is extracted by grinding the roasted seed and boiling the meal with water. The melted fat rises to the top and is skimmed off.

Malabar tallow is free from taste and odour. In the fresh state it has a greenish-yellow colour; on exposure to the air it is rapidly bleached. Its consistence approaches that of mutton tallow. The commercial fat contains about 2 per cent of a pleasantly smelling volatile oil, which can be extracted with alcohol. Two samples of fat examined by *Crossley* and *Le Sueur* [3] had the acid values 5·18 and 15·34 respectively.

[1] Baczewski, *Journ. Soc. Chem. Ind.* 1895, 1049; *Monatsh. f. Chemie*, 1895, 866.
[2] Wagner's *Jahresbericht*, 1884, 1186. [3] *Journ. Soc. Chem. Ind.* 1899 991.

Physical and Chemical Characteristics of Malabar Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Viscosity.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Seconds at 140° F.	Observer.
9·4	0·9102	Dal Sie	30·5	Vierthaler and Bottura	36·5	Vierthaler and Bottura	191·9	Höhnel and Wolfbauer	37·82-39·63	Crossley and Le Sueur	0·22-0·44	Crossley and Le Sueur	101·5-104	Crossley and Le Sueur
15	0·915	Höhnel and Wolfbauer			30 42	Dal Sie Höhnel and Wolfbauer	188·7-189·3	Crossley and Le Sueur						
100 (water at 100=1)	0·8900-0·8907	Crossley and Le Sueur			37-37·5	Crossley and Le Sueur								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.	
° C.	Observer.	° C.	Observer.
54·8	Höhnel and Wolfbauer	56·6	Höhnel and Wolfbauer

The specimen of Malabar tallow examined by *Höhnel* and *Wolfbauer* consisted of 19 per cent of free fatty acids and 81 per cent of glycerides. The solid fatty acids melted at 63·8° C.

In India, Malabar tallow is used as an edible fat.

CACAO[1] BUTTER

French—*Beurre de cacao.* German—*Kakaobutter.* Italian—*Burro di cacao.*

For table of characteristics see pp. 480, 481.

Cacao butter is expressed from the cacao beans, the seeds of the cacao-tree, *Theobroma cacao*, L.[2]

The cacao tree is indigenous to the West Indies. As its cultivation is remunerative, the tree has been introduced into various tropical countries, especially Central and South America. The cultivation of the tree on the West Coast of Africa has also been attended with success, and considerable quantities of cacao beans from Nigeria, etc., are shipped to Europe. At present even vacuum plant is being introduced into the West African cacao plantations, so as to dry[3] the beans in as expeditious a manner as possible before shipping them to Europe. Experiments made in Dahomey with the cultivation of the cacao tree gave very good results, but have not led to commercial success owing to the competition of the neighbouring colonies.

The following tables give some data as to the extent of the production of cacao and the imports into the most important countries[4]:—

Production of Cacao Beans (in kilograms)

	1905.	1906.	1907.
Venezuela . Caracas	6,955,629	6,524,878	7,056,324
Venezuela . Carupano	3,106,864	2,657,637	3,689,471
Ecuador . Guayaquil	1,604,200	20,711,500	18,285,000
Brazil . Bahia	17,123,400	22,681,620	23,361,000
Brazil . Parakako	...	2,104,751	3,517,432
British West Indies . Trinidad	22,520,700	13,262,050	18,869,940
British West Indies . Grenada	5,796,575	4,940,030	3,433,830
British West Indies . San Thomé	29,947,952	28,707,560	28,226,310
Dominican Republic	12,644,952	14,328,482	10,955,650
British West Africa	5,179,054	9,084,314	11,376,608
Other countries (estimated)	30,124,613	33,586,000	26,101,791

[1] I prefer the spelling "cacao" to "cocoa," in order to avoid the confounding of this fat with cocoa nut oil or kokum butter.

[2] For a useful summary of our knowledge regarding the botany, chemistry, and diseases of the cacao-tree, cp. H. Wright, *Theobroma Cacao or Coco*, Colombo, 1907.

[3] A description of a drying house for cacao, erected in Trinidad, is given in the *Quarterly Journal, Institute of Commercial Research in the Tropics* (Liverpool University), vol. ii. 1907, No. 5, 121.

[4] Cp. O. Rohdich, *Inaugural Dissertation*, University, Jena, 1908. (See Appendix.)

Import of Cacao Beans during January to August (in kilograms)

	1905.	1906.	1907.
United States of America . .	43,174,135	...	56,024,400
Germany	49,487,870	51,974,560	53,868,910
France	36,891,950	37,947,410	41,815,600
United Kingdom . . .	22,986,462	25,121,648	23,473,322
Belgium	1,982,782	2,479,026	2,085,997
Holland	26,248,100	31,707,300	32,844,500
Spain	8,484,200	8,615,800	9,200,000

The beans are chiefly worked up for the preparation of cacao; hence cacao butter is to some extent a by-product of this industry.[1]

The cacao beans are roasted[2] over coke fires (similarly as coffee is roasted), and the husks[3] are separated by winnowing. The kernels remaining after winnowing are ground under millstones and reduced to a paste. The bulk of the fat is then removed by hot expression in hydraulic presses. Before the ground material is put into the presses alkali carbonates are added;[4] some manufacturers also add the carbonates before roasting. As the alkali will combine with any free fatty acids, the manufactured product is practically devoid of free fatty acids, and the soaps are likely to pass into the expressed fat. Hence in the examination of cacao butter the presence of ammonia may be expected, and the ash should be determined. *Strube*[5] has shown that the different methods of treating the cacao mass have no influence on the properties of cacao butter.

The proportion of fat in the beans varies from 50 to 56·5 per cent. In determining the fat in the beans great care must be exercised

[1] It is likely that in Germany cacao powders containing less than 20 per cent of cacao butter will have to be declared specially as such. In order to press the cacao bean meal so that the cakes contain less than 20 per cent of cacao butter, it is necessary to subject the mass, after the bulk of the fat has been expressed at a low pressure (say 50 atmospheres) for some prolonged time to a pressure of at least 200 atmospheres in the hot press. According to experiments by Böhme (*Chemiker Zeit.* 1908, 98, 110) it was not possible to obtain a mass containing less than 20 per cent of fat, if the pressure was maintained for a period of 40 minutes only, the lowest percentage having been 20·61 per cent (calculated to dry substance, 21 per cent). In order to obtain a mass containing less than 20 per cent of fat it is necessary to press at 200 atmospheres in the hot for about 1-1½ hours, or to use a higher pressure.

The percentage of fat in the beans has nothing to do with the ultimate content of fat in the expressed mass, for if the beans were very poor in fat, so much less butter would run off in the preliminary expression. In order to prepare cacao mass, which only retains 15-16 per cent of fat (calculated to dry substance), it is necessary to allow a pressure of at least 350 atmospheres or 400 atmospheres for some prolonged time. Cp. P. Welmans, *Pharm. Zeit.* 1907 (52), 891; L. Weil, *ibid.* p. 913; F. Müller, *ibid.* 1908 (53), 57.

[2] The composition of the cacao butter is not affected by the roasting. This has been specially shown by Heiduschka and Herb, *Pharm. Zentralhalle*, 1908, 375, in the examination of cacao fruits which had been preserved in brine.

[3] The husks yield the "shell cacao" for cattle feeding.

[4] Usually a 10 per cent solution of potassium carbonate is employed. As a rule, 1 litre of this solution is added to 100 kg. of cacao mass. Some manufacturers use a litre of ammonia for the same quantity of cacao mass.

[5] *Zeit. f. öffentl. Chem.* 1908, 67.

in disintegrating them. It will be found best to preliminarily extract the bulk of the fat from the finely-divided mass, then to dry, grind up with sand, and exhaust completely.

According to *Davis* and *M'Lellan*,[1] the roasted cacao beans are best extracted with petroleum ether of boiling point 40° C. to 50° C. Common ether extracts 0·2-0·5 per cent more than petroleum ether, theobromine and some colouring matter being dissolved by the common ether. The following percentages of fat were ascertained in roasted nibs by *Davis* and *M'Lellan* :—

Country.	Fat. Per cent.
Ecuador, Arriba	54·66
,, other varieties	52·87
Venezuela, East of Caracas	51·33
,, West of Caracas	53·05
Dutch Guiana, Surinam	56·37
Brazil, Para	54·98
,, Bahia	54·33
Africa, West Coast	54·18
West Indies, Trinidad	54·57
,, Grenada	55·30
,, Dominica	56·03
,, Santo Domingo, "Samana"	55·38
Jamaica	56·57
Ceylon	53·36

These results may be supplemented by some later analyses published by *Genin*.[2] The solvent used for extraction was petroleum ether.

Origin.	Water.	Fat.	Fat calculated to Dry Substance.
	Per cent.	Per cent.	Per cent.
Bahia	2·00	54·60	55·71
Para I.	2·70	55·50	57·04
Para II.	1·80	56·90	57·94
Caracas I.	2·52	52·80	54·16
Caracas II.	2·10	54·70	55·87
Carupano I.	2·50	53·60	54·97
Carupano II.	2·15	54·13	55·32
Trinidad I.	2·84	53·70	55·27
Trinidad II.	2·94	51·70	53·26
Sanchez I.	3·40	53·27	55·14
Sanchez II.	2·12	52·50	53·63
Martinique I.	2·40	54·70	56·04
Martinique II.	2·74	53·20	54·69
Guadeloupe	2·24	54·40	55·64
Santa Lucia I.	2·08	56·10	57·29
Santa Lucia II.	2·53	54·80	56·22
Santa Lucia III.	2·81	53·40	54·94
Grenada I.	3·10	54·20	55·93
Grenada II.	3·05	54·00	55·69
Accra (Africa) I.	2·54	54·90	56·33
Accra (Africa) II.	1·96	53·80	54·87
Congo	2·51	54·90	56·31

[1] *Journ. Soc. Chem. Ind.* 1904, 480.
[2] *Rev. génér. chim. pure et appliq.* 1907 (x.), 303.

The cacao beans destined for the manufacture of best chocolate are roasted and freed from shells, as described above, but are not expressed, so that the full amount of fat remains in the ground mass. This is then mixed with sugar and arrowroot. Some chocolate manufacturers, however, express part of the cacao butter and sell it as such, substituting the amount expressed from the cacao mass by "chocolate fats" (see Vol. III. Chap. XV.).

Cacao butter has a yellowish-white colour, turning white on keeping. It possesses an agreeable taste and pleasant odour like chocolate. At the ordinary temperature it is somewhat brittle.

Amongst the solid cacao butter fatty acids, stearic, palmitic, and arachidic acids have been ascertained. The occurrence of lauric acid is doubtful (cp. *Traub*[1]). Theobromic acid, $C_{64}H_{128}O_2$, stated by *Kingzett*[2] to occur in the fat, is, according to *Graf*,[3] most likely arachidic acid. Stearic acid, first found in cacao butter by *Stenhouse*,[4] occurs to an extent of 39 (*Lewkowitsch*[5]) to 40 per cent (*Hehner* and *Mitchell*[6]). *Farnsteiner* obtained by the barium-salt-benzene method 59·7 per cent of solid acids, 31·2 per cent of oleic acid, and 6·3 per cent of other liquid acids. Linolic acid has been proved to occur in cacao butter by *Benedikt* and *Hazura*.[7] The statement that cacao butter contains formic, acetic, and butyric acids (which was supported by a high *Reichert* value recorded in the older literature) has been shown by the author to be erroneous.

Cacao butter appears to contain considerable amounts of mixed glycerides. *Fritzweiler*[8] isolated from cacao butter about 6 per cent of oleodistearin. *Klimont* stated that he had isolated from cacao butter oleopalmitostearin and oleodipalmitin, but this appeared open to doubt, as his "oleopalmitostearin" had the low melting point of 31·33° C. (against *Hansen's* 42° C.). The renewed examination of cacao butter by *Klimont*[9] himself led him to withdraw his statement with regard to oleopalmitostearin, and he now states that cacao butter contains oleodistearin (found before him by *Fritzweiler*), as also oleodipalmitin (see Vol. I. Chap. I.). On allowing large quantities of "Samana" butter to cool slowly *Strube*[10] obtained a liquid portion, which differs from ordinary cacao butter in that it does not solidify readily. This liquid butter has the following characteristics:—Specific gravity at 17·5° C., 0·906; melting point about 12° C.; iodine value, 53·6-58·8; butyro-refractometer at 40° C., 50·45 "degrees."

Strube[11] observed also a separation of a liquid portion from "Thomé" cacao butter. In this case, however, the liquid portion differed very little from normal cacao butter in its characteristics; only the acid value was found somewhat higher, viz. 7·7.

[1] Wagner's *Jahresbericht*, 1883, 1159. [2] *Journ. Chem. Soc.* 1878, 38.
[3] *Arch. Pharm.* 1888, 830. [4] *Liebig's Annal.* 36 (1840), 56.
[5] Unpublished observations. [6] *Analyst*, 1896, 328. [7] *Monatshefte*, 1889, 353.
[8] *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1902, 371.
[9] *Monatsh.* 1905, 563. [10] *Zeit. f. öffentliche Chemie*, 1905, 215.
[11] *Ibid.* 1908, 67.

Matthes and *Rohdich* [1] examined the unsaponifiable matter of cacao butter. They obtained from 13 kilograms of fat 28 grams of crude unsaponifiable matter, which yielded 22 grams of "crude phytosterol," and 6 grams of an ethereal oxygen-containing oil, smelling of hyacinths. The refractive index of this oil at 40° C. was 1·492, the iodine value 68·58, and the optical rotation + 0·37° in 10 per cent benzene solution (the length of the tube is not stated).

The crude phytosterol consisted of a hydrocarbon of the composition $C_{30}H_{48}$ (most likely identical with amyrilene), stigmasterol (identified by the tetrabromo-derivative of its acetate), and (phytosterol or) sitosterol (identified by the melting points of its acetate, viz. 130° C., and of the dibromo-derivative of its acetate, viz. 135° C.). In a later communication [2] *Matthes* and *Rohdich* state that the two alcohols obtained from the tetrabromo- and the dibromo-derivatives melted respectively at 162-163° C. and at 139° C.

In the pharmaceutical literature the statement was frequently made, and is still being copied into text-books, that cacao butter does not turn rancid. *Dieterich* contradicted this statement some years ago; the author then showed by an extended series of observations [3] that cacao butter does turn rancid like any other fat under conditions favouring hydrolysis and subsequent rancidity. The author proved this in a somewhat exaggerated manner by exposing fresh cacao butters to the atmosphere in sunlight, when rancidity set in within a few (three to four) days. It must be left undecided whether the older erroneous statements, based on somewhat limited experience, are due to the fact that cacao butter, owing to its high price, is kept in a more careful manner than ordinary fats, or whether the keeping properties are due to the aromatic substance in cacao butter, which retards the setting in of hydrolysis (much as lard is preserved by "benzoating," *i.e.* by suspending powdered benzoin in the melted fat and allowing it to remain therein for some time).

The statement that rancid cacao butter is obtained from mouldy beans is erroneous. Most shipments of cacao beans become mouldy in transit, but since the beans, in the first stage of manufacture, are roasted, the mould is destroyed, so that cacao butter prepared from these beans need not of necessity become rancid.

The acid value of commercial samples of cacao butter was found by *Dieterich* to be from 1 to 2·3. *Lewkowitsch* found in a large number of genuine fresh cacao butters acid values varying from 1·1 to 1·95. A sample that had been kept ten years in a sealed bottle had the acid value 4·6.

On account of its high price cacao butter is frequently adulterated and also wholly substituted by chocolate fats (see Chap. XV.). The latter consist chiefly of the "stearine" of cocoa nut and palm nut oils. They are readily differentiated from cacao butter by their *Reichert-Meissl* values, and especially by their low iodine values.

[1] *Berichte*, 1908, 19. [2] *Ibid.* 1908, 1592.
[3] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1899, 557.

Physical and Chemical Characteristics of Cacao Butter

Specific Gravity.[1]			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.		
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At ° C.		Observer.
15	0·964-0·976	Dieterich	25-26	Herbst	32-34	Hager	192-202	Filsinger.	34	Hübl	0·2 [3]	Lewko-	60	1·4496	Thoerner
20	0·9702	Rakusin	27·3	Rüdorff	32·1-33·6	Filsinger	193·55	De Negri	34-37·5	Filsinger		witsch	40	1·4565 to	Strohl
50	0·8920	Allen	23-21·5	De Negri	30-32	Dieterich		and Fabris	36·62	De Negri	0·5 [4]	,,		1·4578 [2]	
(water 15·5 = 1)				and Fabris	30-34	,,	198-200	Thoerner		and Fabris	0·33-	,,			
98	0·8577	,,	23	Thoerner	33·5	Rüdorff	191·8-	Lewko-	32·8-41·7 [2]	Strohl	0·38 [5]				
(water 15·5 = 1)					28-30	De Negri and Fabris	194·5	witsch	34·3-37 [6]	Lewko- witsch	0·83 [7]	,,	Butyro-refractometer.		
					32-33	Thoerner							At 40° C. "Degrees."		Observer.
					28-33	Lewko- witsch							46-47·8		Strohl
													46-46·5		Mansfeld

[1] According to *White* (*Pharm. Journ.* 1898, 69) the specific gravity of cacao butter, when freshly melted, rises gradually from 0·950 until it reaches its highest value 0·995 after a few days.

[2] Forty commercial samples. [3] Genuine cacao butter, kept ten years in a sealed bottle. [4] Prepared in the laboratory from nibs.

[5] Genuine English cacao butters, fresh. [6] From nearly 100 samples. [7] Genuine Dutch cacao butter, fresh.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
94·59	Bense-mann	51	Hübl	52	Hübl	190	Thoerner	39·1	De Negri and Fabris	1·422	Thoerner
				48-49 / 51-52	Bense-mann						
				49-50 / 52-53	,,			32·6	Thoerner		
		47-45	De Negri and Fabris	48-50	De Negri and Fabris						
		46-47	Thoerner	49-50	Thoerner						
		Titer Test.									
		48·3	Lewko-witsch								
		49·2	,,								
		49·6	,,								

Less decisive are the indications furnished by the melting point of the fat itself; in this connection it should be noted that the freshly melted cacao butter shows a considerably lower melting point than the normal one, and only regains its normal (higher) melting point when the sample has been kept for several days (in a desiccator). When determining the melting point it is best to proceed as described in Chapter V.[1]

For the detection of "chocolate fats" (sold under various fancy names, see Chap. XV.) in genuine cacao butter, the determination of the saponification value and of the iodine value will as a rule suffice. These substitutes considerably raise the saponification value, whilst they lower the iodine value. The "titer" test of the fatty acids is also considerably depressed by them. The determination of stearic acid may be carried out as a confirmatory test. It is then hardly necessary to determine the *Reichert-Meissl* value. Therefore, the proposal made by *Wauters*[2] to ascertain the presence of cocoa nut oil in cacao butter in the same manner as is done in butter fat (see "Butter Fat") would appear to be an unnecessary process.

The presence of vegetable oils, such as *almond oil*, *arachis oil*, *sesamé oil*, *hazel nut oil*, would be readily recognised, in the first instance, by an increase in the iodine value, and by the lowering of the solidifying and melting points of the insoluble fatty acids.

Bees' wax and paraffin wax (stated to have been employed as adulterants) will hardly be added now, as they are too easily detected (by a low saponification value and a considerable amount of unsaponifiable matter). The presence of bees' wax would also be indicated by a high acid value of the sample. Cacao butters of comparatively high acid values owe their acidity (in the absence of adulterants) either to rancidity (ascertainable by the taste), or to admixture with fat which has been extracted from cacao bean shells. Very likely the cacao butters in which *Filsinger* found as much as 28 per cent of free fatty acids had such an origin.[3]

The most difficult problem was, until recently, to detect adulteration with tallow. *Hager's* aniline test, recommended for that purpose, has been found useless by the author; its description is therefore omitted here.[4]

Björklund's ether test may be recommended as a preliminary test. It is carried out as follows[5]:—Place about 3 grms. of the sample in a test-tube, add twice the weight of ether at the temperature of 18° C., close the test-tube with a cork, and effect solution, if possible, by shaking. The fat should dissolve to a clear solution. Then immerse the tube in water at 0° C., and note the number of minutes which the liquid requires to become milky, or to deposit white flocks, and observe the temperature at which the solution becomes again clear when removed from the water. The following table gives *Björklund's*

[1] Cp. also Welmans, "Ueber Oleum Cacao," *Pharm. Zeit.* 1900, 99.

[2] *Bulletin de l'Association Belge des Chimistes*, 1901, vol. xv. No. 3, March.

[3] "Cacao (cocoa) shell butter" is obtainable as an article of commerce.

[4] See 2nd edition of this work, p. 529.

[5] *Zeit. analyt. Chemie*, 3. 233.

observations made on pure cacao butter and on samples mixed with tallow :—

	Turbidity at 0° C. after Minutes	Clear Solution at ° C.
Pure cacao butter	10-15	19-20
Cacao butter + 5 per cent of beef tallow .	8	22
Cacao butter + 10 per cent of beef tallow .	7	25

The author[1] found, however, that cacao butters containing as much as 10 per cent of tallow will dissolve in two parts of ether at 18° C., although requiring a little longer time than genuine cacao butter does. The chief indication to be relied upon is not, therefore, the number of minutes required for crystallisation—as the time will vary for different samples—but the characteristic way in which genuine cacao butter crystallises as compared with adulterated samples. In the former case tufts of distinct crystals appear at the bottom and the sides of the containing vessel, whereas five or more per cent of tallow are recognised by flocks separating from the cooled solution.

The modification of *Björklund's* test recommended by *Filsinger*, viz. to dissolve 2 grams of the sample in 6 c.c. of a mixture of 4 parts of ether and 1 part of alcohol, is scarcely an improvement, and cannot therefore be recommended.

A reliable method to detect the presence of tallow is afforded by the isolation of cholesterol from the unsaponifiable matter by means of its dibromide, and further by the phytosteryl acetate test. The microscopic examination for the presence of cholesterol crystals will not furnish decisive information (*Lewkowitsch*).[2]

The statement by *Sachs*[3] that Borneo tallow is used as an adulterant of cacao butter requires confirmation.

Cacao butter is a by-product in the manufacture of cocoa, and is therefore obtainable in large quantities. It is used in the manufacture of chocolates,[4] in confectionery, in pharmacy (nitro-glycerine tablets), and in the preparation of perfumes.

CHINESE VEGETABLE TALLOW

French—*Suif végétal de Chine.* German—*Chinesischer Talg ; Stillingiatalg ; Vegetabilischer Talg.* Italian—*Sego di Stillingia.*

For tables of characteristics see pp. 485-487.

Vegetable tallow is the hard fat which coats the seeds of the Chinese tallow tree, *Stillingia sebifera*, Willd. (*Stillingia sinensis, Croton*

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1899, 557. [2] *Ibid.*
[3] *Chem. Rev.* 1907, 279.
[4] The introduction of additional cacao butter over and above the natural proportion in the beans permits the incorporation of a larger amount of starch than can be added to the genuine cacao mass in the manufacture of chocolate.

sebiferum, *Sapium sebiferum*, Roxb., *Excœcaria sebifera*, F. Müll., *Carumbium sebiferum*).[1] The tree grows wild in China.[2] Since it has been cultivated there, it has been introduced into Indo-China and the north of India, where it thrives luxuriantly. The tree has also been introduced into South Carolina. In China the stillingia tree is regularly exploited for both its leaves and seeds; the fat, however, represents a secondary product only. In Tonkin the tree is only cultivated for the sake of its leaves, a decoction of which furnishes a colouring matter used for dyeing silk.

The tree commences to produce at the age of four to five years, and when it has reached its full development, it yields about 25-30 kilos. of seed a year. 100 kilos. of the fruit yield about 30 kilos. of *mou-iéou* (*i.e.* vegetable tallow + stillingia oil), or 15 kilos. of *pi-yu* (*i.e.* vegetable tallow) and 15 kilos. of *tsé-tiéou* or *ting-yu* (*i.e.* stillingia oil).

The fruit contains three oval seeds surrounded by a thick tallow-like mass. The seeds themselves contain a brownish-yellow oil, which has been described already (p. 70) under the name of stillingia oil. *Tortelli* and *Ruggeri*, who prepared the solid fat and the oil from the seeds separately, obtained 22 per cent of vegetable tallow and 19·2 per cent of stillingia oil. According to *Lemarié* (Director of Agriculture, Annam), the seeds of *Sapium sebiferum*, known locally as "*cây-sói*," yield 69 per cent of shells and 31 per cent of kernels. The shells are coated with 29·5 per cent of a white solid fat, and the kernels contain 59·5 per cent of oil. *Schindler* and *Waschata*[3] found 36·4 per cent of vegetable tallow on the entire seed.

According to the process of manufacture employed, three products are obtained. One process has for its object the separate production of vegetable tallow and of stillingia oil. The seeds are either placed in perforated cylinders and steamed, so that the fat melts and runs off, or they are passed between fluted rollers which scrape off the outer fat-coating without breaking the seed proper, when the scraped-off mass is pressed in the hot in primitive wedge-presses. This product is sold under the Chinese name "*pi-iéou*," or "*pi-yu*," and is known to the European candle-makers as "prima" vegetable tallow. The seeds are then removed and crushed separately for the recovery of the stillingia oil, *tsé-tiéou* or *ting-yu* (see p. 70).

In the second process the seeds, together with their coating of fat, are crushed, and a mixture of vegetable tallow and stillingia oil is thus obtained. The product from the latter process is naturally much softer than the true vegetable tallow; it has a lower melting point, and also a much higher iodine value. This second quality is sold under the name "*mou-iéou*," known to the European candle-makers as "secunda" vegetable tallow, and represents a mixture of "*pi-yu*" and "*ting-yu*."

[1] *Bull. Imperial Institute*, 1903, 209; "Les arbres à suif de l'Indo-Chine," *Bull. économ.* 1902, Hanoi. (See Appendix.)

[2] It is known by the name Mu-tsé-shou.

[3] *Zeit. f. das landw. Versuchsw. in Oesterr.*, 1904, 643.

Physical and Chemical Characteristics of Vegetable Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.
15	0·918	Thomson and Wood	26·7	Thomson and Wood	44·5	Thomson and Wood	200·3 [3]	Lewkowitsch
15	0·915	Lemarié [1]	24·2-26·2 [3]	Lewkowitsch	43-46 [3]	Lewkowitsch	179 [3]	De Negri and Fabris
50	0·915	Jules Jean [2]	34 [3]	De Negri and Fabris	44 [3]	De Negri and Fabris	203·6 [3]	Hobein
			35 [3]	Hobein	35	Lemarié [1]	203·3 [4]	,,
			32 [4]	,,	43-45	Hobein	199-202·2 [5]	De Negri & Sburlati
			27·2-31·1 [5]	De Negri & Sburlati	39-42	,,	203·5	Klimont
100 (water 15=1)	0·8600	Zay and Musciacco	37·7	Zay and Musciacco	36·5-44·1 [5]	De Negri & Sburlati	231	Zay and Musciacco
					53·2	Jules Jean		
					36·4	Klimont		
					52·5	Zay and Musciacco		

[1] *Mou-iéou* oil. [2] *Zeit. ang. Chem.* 1898, 250. [3] Commercial sample. [4] Prepared from the seeds by steaming.
[5] Ten samples of commercial fat; the lower melting fats no doubt consisted of *mou-iéou* oil.

Physical and Chemical Characteristics of Vegetable Tallow—continued

Iodine Value.		Reichert-Meissl Value.		Refractive Index.		
				Oleo-refractometer.		
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	"Degrees."		Observer.
32·1-32·3 [1]	Lewkowitsch	0·69	Zay and Musciacco	−23		Jules Jean
22·87	Hehner and Mitchell					
35·5 [1]	Hobein					
28·5 [2]	,,			Butyro-refractometer.		
28·5-37·7 [3]	De Negri & Sburlati					
38·3	Jules Jean			At °C.	"Degrees."	
19·0	Zay and Musciacco					
27·6	Klimont			50	38	Zay and Musciacco

[1] Commercial sample. [2] Prepared from the seeds by steaming.
[3] Ten samples of commercial fat ; the lower melting fats no doubt consisted of *mou-iéou* oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
		Titer Test.							
93·45	Zay and Musciacco	52·1-53·5 [1]	Lewkowitsch	56-57	Mayer	182·1 [1]	De Negri and Fabris	34·2-34·3 [1]	Lewkowitsch
		42 [1]	De Negri and Fabris	47 [1]	De Negri and Fabris	207·9 [1]	Hobein	47 [1]	De Negri and Fabris
		41 [1]	Hobein	51 [1]	Hobein	206·4 [2]	,,	54·1-54·8	,, ,,
		40 [2]	,,	49 [2]	,,	202-208·5 [3]	De Negri and Sburlati	38·1 [1]	Hobein
		45·2-47·9 [3]	De Negri and Sburlati	53-56·9 [3]	De Negri and Sburlati	240·1 (!)	Zay and Musciacco	29·2 [2]	,,
		56·4	Jules Jean	56·8	Jules Jean			30·3-39·5 [3]	De Negri & Sburlati
								Liquid Fatty Acids.	
								97·04	Zay and Musciacco

[1] Various commercial samples.

[2] Prepared from the seeds by steaming.

[3] Ten samples of commercial fat ; the lower melting fats no doubt consisted of *mou-iéou* oil.

Samples of vegetable tallow which have been prepared in the laboratory by extracting the crushed fruit with solvents, contain therefore stillingia oil, and such numbers as were given by *De Negri* and *Fabris* for vegetable tallow extracted by them from the seeds by means of ether and carbon bisulphide do not hold good for true vegetable tallow. Hence numbers referring to a mixture of vegetable tallow and stillingia oil have been omitted from the tables; nor have numbers observed for commercial fats, which undoubtedly represent a mixture of the two kinds of products, been recorded here.

Crushed vegetable tallow, if free from stillingia oil, leaves no grease-spot on paper. The samples examined in the author's laboratory had acid values varying from 7·07 to 7·51. *De Negri* and *Fabris* found 2·4; *De Negri* and *Sburlati*,[1] 2·2; *Klimont*, 14·2; *Zay* and *Musciacco*, 22·5.

According to *Maskelyne*, vegetable tallow consists of palmitin and olein. A confirmation of this statement may be found in the fact that *Hehner* and *Mitchell*[2] obtained no stearic acid crystals from a specimen absorbing 22·87 per cent of iodine. This is further confirmed by *Klimont*,[3] who found in a commercial sample (of the iodine value 27·6) palmitic and oleic acids only. *Klimont*[4] is of the opinion that oleodistearin occurs in this fat.

On repeatedly crystallising vegetable tallow from acetone (*Klimont*),[5] oleodipalmitin was obtained. In *Klimont's* opinion, vegetable tallow consists chiefly of oleodipalmitin, with smaller quantities of tripalmitin.

Zay and *Musciacco* state that the mean molecular weight of the insoluble fatty acids is 231·4, and that they isolated volatile fatty acids of the molecular weight 132·8. The low molecular weight of the insoluble fatty acids would point to the presence of lauric acid. The number 231·4 stands in need of confirmation.

The production of vegetable tallow in China is very large, and has been practised there for many centuries. The fat is used there extensively for the manufacture of candles. Hankow is the central market whence the bulk of Chinese tallow is shipped. Before the material reaches Hankow it undergoes, at Tchang-té-fou, the first manipulation, consisting in the mixing of the *mou-iéou* with the *pi-yu*. Thus the intermediate quality is obtained, known as "secunda vegetable tallow," whilst the pure *pi-iéou* is termed "prima quality." At Hankow it undergoes the final process, consisting in the re-melting of the fat, and the freeing of it from foreign substances which have been added fraudulently; it is then cast into blocks, in which form the fat is received on the European market. The first considerable quantities came into the European market in 1894. The latest statistics available report that in the year 1903 about 7039 tons, and in the year 1904 about 5000 tons, were exported. In 1905 the exportation is stated to have amounted to 5250 tons (87,500

[1] De Negri and Sburlati, *Journ. Soc. Chem. Ind.* 1897, 339.
[2] *Analyst*, 1896, 328.
[3] *Monatshefte f. Chemie*, 1903, 408.
[4] *Ibid.* 1905, 563.
[5] *Ibid.* 1903, 408.

piculs). The Custom officers in Hankow state that at least an equal quantity is registered for home consumption, so that the total production may be taken as 10,000 tons per annum. The chief countries which import vegetable tallow are Italy, the United Kingdom, and France. Small quantities only are bought by the United States. Only the two qualities *mou-iéou* and *ting-yu* are exported.

KOKUM BUTTER, GOA BUTTER, MANGOSTEEN OIL

French—*Beurre de kokum.* German—*Kokumbutter.*
Italian—*Sego di kokum.*

For tables of characteristics see p. 490.

This fat is obtained in the East Indies from the seeds of the Guttifera, *Garcinia indica*, Choisy, *Garcinia purpurea*, Roxb. (*Mangostana indica*, L., *Brindonia indica*, Du Pet.). The seeds contain 20-25 per cent of fat.

The fat is prepared in India—especially at the west coast, between Daman and Goa—in a primitive fashion, by drying the seeds in the sun and boiling them out with water. The fat is then skimmed off, filtered in a crude fashion, and cast into round cakes weighing about 100 grams each. This is the form in which the kokum butter is sold in the Indian bazaars.

Kokum butter is a white or light grey fat, having a slight, not disagreeable odour, and a mild oily taste.

The acid constituents of kokum butter are oleic and stearic acids, with small quantities of (probably) lauric acid. According to *Heise*[1] (confirmed by *D. Hooper*[2]), this fat (like Mkányi fat) consists chiefly of oleodistearin. The specimen examined by *Heise* contained 10·5 per cent of free fatty acids, and that tested by *Crossley* and *Le Sueur*[3] 7·1 per cent, calculated as oleic acid.

Kokum butter is chiefly used as an edible fat, and is stated to be employed for the adulteration of "ghee butter." It is also used in pharmacy for ointments, etc. The kokum butter which is unfit for edible purposes is worked up for soap.

Other species of *Garcinia* (cp. "Gamboge Butter," p. 451) yield similar fats, which have not been examined fully, such as—

(1) The fat from *Garcinia pictoria*, Roxb. This fat is chiefly obtained in the western district of Mysore, where it is used as an edible fat by the poorer classes. The bulk of the fat which has become rancid, being unfit for consumption, is used as a burning oil.

[1] *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1896, 13. 302.
[2] *Journ. and Proceedings of the Asiatic Soc. of Bengal*, 1907, iii. 257-259.
[3] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Characteristics of Kokum Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At °C.		Observer.
40 (water 15° = 1)	0·8952	Heise	33·3	Redwood	36·7	Redwood	191·3	Heise	33·1	Heise	1·54	Heise	25	1·4628 [2]	Heise
			27·5	Flückiger and Hanbury	42·5-45	Flückiger and Hanbury	186·8	Crossley and Le Sueur	34·2	Crossley and Le Sueur	0·11	Crossley and Le Sueur	40	1·4565 [2]	Crossley and Le Sueur
98 (water 15° = 1)	0·8574	,,	37·6-37·9	Heise [1]	41-42	Heise [1]									
100 (water 100° = 1)	0·8889	Crossley and Le Sueur			42	Crossley and Le Sueur									
					43	Hooper	191·5	Hooper	25	Hooper	0·98	Hooper			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.	Melting Point.	Mean Molecular Weight.	Observer.
Per cent.	Observer.	°C.	°C.		
95·59	Heise	59·4	60-61	282	Heise
94·59	Crossley and Le Sueur				
93·5	Hooper	...	61	...	Hooper

[1] The melting point varied according as to whether the melted fat was allowed to solidify rapidly at 0° C., or kept at the ordinary temperature; in the former case the melting point was 32°-33° C., in the latter it rose to 40° C. after 24 hours' standing (cp. Chap. V.).

[2] Calculated from observations made with the butyro-refractometer.

(2) The fat from *Garcinia tonkinensis*, Vesqu. (*Garcinia Balansæ*, H. Baillon), the *Cáy gioc* or *Cáy doc* of the Annamites. It is stated to have the iodine value 67·14, the saponification value 198·3 (the specimen having the acid value 93) to contain 4·6 per cent of an ethereal oil, and nearly 6 per cent of resinous substances[1] (these numbers require confirmation). The fat is used as a burning and as a lubricating oil.

(3) *Garcinia echinocarpa*, locally known in India as "madol oil."[2] The seeds yield a thick oil, which is used as a burning oil, and also for medicinal purposes (as a vermifuge).

BORNEO TALLOW[3] (TANGKAWANG FAT)

French—*Suif végétal de Bornéo.* German—*Borneotalg.*
Italian—*Sego di Borneo.*

Borneo tallow is obtained from the kernels of a large variety of plants belonging to the family of *Dipterocarpus*, as *Shorea stenoptera*, Burck., *Shorea aptera*, Burck., *Hopea aspera*, de Vriese, *Isoptera borneensis*, Scheff., *Pentacme siamensis*, Kurz, etc., indigenous to the Sunda Islands and Indo-China.[4] The native name of Borneo tallow is Minjak Tangkawang (Tangkawang Fat). The "minjak tangkawang" represents a mixture of at least six fats, obtained from six varieties of trees, known to the natives as *Tangkawang toengkoel*, *T. rambei*, *T. lagar* (these trees have a diameter of more than 3 ft.), *T. goentjang* (growing in swampy regions and reaching a height of 22 ft., whilst the diameter of the trunk rarely exceeds 6 inches), *T. madjan*, *T. terindak*. The last two trees bear smaller fruits, which yield a fat containing about 3 per cent of unsaponifiable matter, which is apparently a natural rosin, inasmuch as it imparts to the fat a viscous character. The first four trees grow wild on the west coast of Borneo, excepting on the strips of land bordering the Kapoea River. The "tangkawang trees" are also cultivated by the natives (chiefly in the districts of Sanggan and Sekadan). The trees flower in September and October, and the fruits ripen in February and March.[5]

The fat is prepared by the Annamites, according to *Lemarié*, in the following manner:—The hard fruits are left for some time in a damp place until the shells break and the seeds begin to germinate. They are then dried in the sun, and the kernels are separated from the pericarp and placed in baskets of bamboo canes, which are suspended over pots of boiling water. When the kernels have become soft and pasty, they are placed in bags and pressed. The fat thus obtained is moulded in the internodes of bamboo stems; hence the commercial samples have a cylindrical shape.

[1] Heim, *Moniteur officiel du Comm.* 1901, August; *Bull. économ. de l'Indo-Chine.* Nouvelle série, No. 51.
[2] *Imper. Inst. Journ.* 1901, June. [3] Geitel, *Journ. Soc. Chem. Ind.* 1888, 391.
[4] Pierre, *Flore forestière de la Cochinchine*, 1902.
[5] O. Sachs *Chem. Rev.* 1907, 278.

In Borneo the fat is obtained either by "wet process" or by a "dry process."[1] The wet process consists in placing the fruits in baskets, which are then completely immersed in water; care being taken that the fruits cannot float to the surface, this being done to prevent germination. The immersion in water appears to be a process of preservation, the natives believing that in consequence of this process the fruits are not so easily attacked by the "boebuk" worm. After thirty to forty days the fruits are taken out of the water and the shells are removed. The kernels, which generally split up into four parts, are spread on boards and exposed to the sun to dry. In order to prevent absorption of moisture the fruits are either covered during the night or taken into tents. The dry kernels are termed "paddi-tangkawang."

The "paddi" obtained by a dry process, such as described, p. 491 (a process which is also in vogue in some districts of Borneo, *e.g.* Landak), is stated by the natives to furnish an inferior kind of product. The following are the essential features of a third process (practised in Sanggan): — Immediately after collecting the fruit, the kernels are cut into discs, dried by exposure to the sun, and pressed as described above. This process yields the so-called "tangkawang soentie." This latter quality is considered the best, and is used exclusively for edible purposes by the natives. It is impossible to give the percentage yield of fat from the fruits; it can only be stated that those from *Shorea stenoptera* yield about 50 per cent of fat.

In view of the great commercial importance Borneo tallow may acquire, further investigation is desirable. In commerce, varieties of Borneo tallow are known under the names "Pontianak," "Sarawak," and "Siak" tallow. The "Pontianak" and "Sarawak" are obtained from the first four kinds of tangkawang mentioned above, and are notable for their hardness. Of the two kinds, "Pontianak" is the more valued. The "Siak" tallow is much softer and hence the less valued.[2]

In the following table I give some characteristics of the fats from *Shorea aptera*, *Isoptera borneensis*, and of samples of unknown origin :—

[1] O. Sachs, *Chem. Rev.* 1907, 278.

[2] A variety of Illipé butter is also known in commerce as Siak tallow.

[TABLE

Physical and Chemical Characteristics of Borneo Tallow (Tangkawang Fat)

Fat from	Specific Gravity at 100° C.	Melting Point. °C.	Solidifying Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Observer.
Shorea aptera . . .	...	31	...	191·2	15[1]	Heim
Isoptera borneensis . .	...	...	...	192·2	16[2]	,,
Commercial samples . .	...	35·36 ; 42	...	...	31[3]	Geitel
,, ,, . .	...	34·5-34·7	...	194·6	30·1	Klimont[4]
,, ,, . .	...	42-45	...	193·8	29·4	Farnsteiner[5]
,, ,, . .	0·892	37·5	22	192·4-196	30-31	Sachs

[1] Calculated from Heim's statement that the sample contains 16·7 per cent of oleic acid.
[2] Calculated from Heim's statement that the sample contains 18 per cent of oleic acid.
[3] Calculated from Geitel's statement that the sample contains 34 per cent of oleic acid. [4] *Monatshefte*, 1904, 929.
[5] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1906, xi. 198. Butyro-refractometer at 40° C., 45 degrees. The phytosterol of the fat gives an acetate melting after the sixth crystallisation at 126° C.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Fat from	Insoluble Acids +Unsaponifiable. Per cent.	Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value. Per cent.	Observer.
Shorea aptera . . .	95·5	51	55	268	...	Heim
Isoptera borneensis . .	95·3	51	55	256	...	,,
Commercial samples . .	95·7	53·5-54	...	283·7	...	Geitel
,, ,, . .	...	52	53·5	273·5	31·5	Sachs

Borneo tallow has a light green colour, changing to yellow, and after prolonged exposure to the air, to white. At the ordinary temperature it resembles cacao butter in consistence, as also in taste. It has a crystalline, granular structure, and is covered with fine white needles of stearic acid, the quantity of which amounted, in the case of the specimen examined by *Geitel*, to 9·5-10 per cent. This specimen commenced to melt at 35-36° C., and liquefied completely at 42° C. The solidifying point of the insoluble fatty acids was 53·5-54° C.; they consisted of 66 per cent of stearic and 34 per cent of oleic acids. The somewhat low solidifying point of the mixed fatty acids would seem to indicate the presence of palmitic acid. The probable iodine value of the fat, calculated from the last given figure, is about 31. Borneo tallow is therefore placed next to kokum butter.

By crystallising Borneo tallow from acetone *Klimont*[1] obtained the mixed glycerides oleodistearin and oleodipalmitin.

Borneo tallow is employed by the natives for edible purposes; in Manila it is used for the manufacture of candles. It is exported to Europe, and should prove a valuable material for soap and candle making. The statements that it is also used for "stiffening" edible cocoa nut oil (*Fritzweiler*), and for adulterating cacao butter (*Sachs*), require confirmation.

Cocoa Nut Oil Group

The fats belonging to the cocoa nut oil group differ from most other vegetable fats by their high saponification values. These are due not only to a large amount of lauric acid, but also to a certain proportion of volatile acids, amongst which the "water-insoluble" acids predominate. Hence these fats are characterised by elevated *Reichert-Meissl* values.

The considerable proportion of volatile acids which the fats belonging to this group contain, brings them into relationship with the milk fats of the mammals; but they differ from the latter essentially, not only with respect to their vegetable origin (and, consequently, by the presence of phytosterol as against cholesterol in the milk fats), but also in that they do not contain *butyric* acid. It is due to the proportion of volatile acids in the members of this group that they can be differentiated from other vegetable fats, which contain considerable amounts of lauric acid, and which, therefore, are also characterised by high saponification values. (These latter fats are comprised in a separate group, the most prominent member of which is dika fat. See "Dika Fat Group.")

Owing to their peculiar chemical composition (simulating to some extent that of butter fat) these oils are not readily saponified by weak caustic lyes. They require for saponification alkaline lyes of high

[1] *Monatshefte*, 1904, 929.

strength, and are thereby so easily converted into soap that it is only necessary to stir the fats and caustic alkali together at 30-35° C., and allow the mixture to stand. After some time saponification will take place with liberation of heat. (*Soap-making by the cold process.*) The soaps thus formed are very hard, and combine with a large amount of water without becoming soft. These soaps have further the remarkable property of requiring large quantities of salt to throw them out of their aqueous solution, hence they are used as "*marine soaps.*"

The following fats—arranged in the order of their iodine values—are included in this group :—

(*a*) Muriti fat.
(*b*) Mocaya oil.
(*c*) Cohune oil.
(*d*) Maripa fat.
(*e*) Aouara kernel oil.
(*f*) Palm nut oil.
(*g*) Cocoa nut oil.
(*h*) Fat from *Cocos acrocomoides.*
(*i*) Tonka butter.

(*a*) MURITI FAT[1]

French—*Huile de Muriti.* German—*Muritifett.*
Italian—*Burro di Muriti.*

Muriti fat is obtained from *Mauritia vinifera*, Mart. (*Acrocomia vinifera*, Oerst.), a South American palm. The seed kernels are slightly roasted by the natives, ground to a paste, then slightly warmed by exposing to steam escaping from boiling water, and expressed in sacks between warmed iron plates. The fat has a pleasant taste, and is similar to cocoa nut oil.

Physical and Chemical Characteristics of Muriti Fat

Specific Gravity at 25° C.	Melting Point. °C.	Solidifying Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl-Value.
0·9136	25	17	246·2	25·2	5

The specimen examined by *Fendler*[1] was prepared from a Nicaraguan fruit which yielded 48·7 per cent of fat, having an acid value of 1·69. The melting point of the fatty acids, obtained from three specimens, was 54·5° C. ; it is therefore likely that the fat contains myristic acid.

[1] *Zeit. f. Unters. Nahrungs- und Genussm.* 1903, 1025.

The statement that this fat is also prepared in Trinidad, Jamaica, and Brazil, and has an odour of violets and a sweetish taste, requires confirmation, and seems to be due to confusion with ordinary palm oil. This opinion of the author is confirmed by the further statement that this fat is sold in the localities named as palm oil (cp. "Aouara Oil," p. 498).

(*b*) MOCAYA OIL,[1] MOCAYA BUTTER, MACAJA BUTTER

French—*Huile de mocaya.* German—*Mocayaöl, Macaja butter.* Italian—*Burro di mocaya.*

Mocaya oil is obtained from the kernels of *Acrocomia sclerocarpa*, Mart. (*Cocos sclerocarpa, Cocos aculeata*, Jacq., *Bactris minor*, Gärt.), a palm tree occurring in Paraguay and forming there vast forests. The kernels contain 60-70 per cent of a fat, which greatly resembles cocoa nut oil in its colour, odour, and consistence.

Sack[2] describes this fat under the local name "kaumakka," and as originating from the Surinam maccasuba palm (*Acrocomia sclerocarpa*, Mart.). According to *Sack* the kernels yield only 24·8 per cent of fat, melting at 32·5° C. The fatty acids are stated to consist of 17·5 per cent of oleic and 82·5 per cent of lauric acids. Evidently *Sack* has overlooked the occurrence of volatile fatty acids.

Physical and Chemical Characteristics of Mocaya Oil

Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Iodine Value. Per cent.
22	24-29	240·6	7·0	24·63

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Soldifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.
22-20	23-25	254
		Neutralisation Value of the Non-volatile Acids. Mgrms. KOH.
		244·8

[1] De Negri and G. Fabris, *Giorn. farmac.* 1896, No. 12; *Chem. Rev.* 1897, 82.
[2] "Inspectie van den Landbouw in West Indie," *Bulletin*, No. 5, 1906.

(*c*) COHUNE OIL

French—*Huile de cohune.* German—*Cohunenussöl.*
Italian—*Olio di cohune.*

This oil is obtained from the kernels of the cohune palm, *Attalea cohune*, Mart., which grows abundantly in British Honduras, Guatemala, and Mexico.[1]

The kernels have the appearance of small cocoa nuts; their size is not greater than that of large nutmegs. They contain 40 per cent of a solid yellow fat, resembling in general appearance palm nut and cocoa nut oils.

The mixed fatty acids melt between 27° and 30° C. The *Reichert-Meissl* value of the specimen of cohune oil described in the table had not been determined, but (judging from the high saponification value) that number will very nearly approach the *Reichert-Meissl* values of the other members of the cocoa nut oil group.

Owing to the extreme hardness of the husks, the commercial exploitation of the cohune nuts, which are readily obtainable in large quantities, has hitherto not been taken in hand.

It is doubtful whether the fat from the kernels of the Surinam *Bactris plumeriana*, Mart. (German—*Affendornfett*), known under the native name "keekeesiamakka," and described by *Sack*,[2] is identical with cohune oil. The kernels are stated by *Sack* to contain 34·8 per cent of a fat melting at 32° C., the fatty acids of which are said to consist of 13·6 per cent of oleic and 84·6 per cent of lauric acids. It will be observed that in this case also no mention is made of volatile fatty acids by *Sack*.

Physical and Chemical Characteristics of Cohune Oil

Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
°C. 16-15	°C. 18-20	253·9-255·3[3]	12·9-13·6

(*d*) MARIPA FAT[4]

French—*Huile de maripa.* German—*Maripafett.*
Italian—*Sego di maripa.*

For tables of characteristics see p. 498.

Maripa fat is obtained from the kernels of *Palma* (*Attalea*) *maripa*, Aubl., a plant belonging to the palm family. It is

[1] *Bull. Imper. Inst.* 1903, xxv.

[2] "Inspectie van den Landbouw in West Indie," *Bulletin*, No. 5, 1906.

[3] The original stated erroneously saponification "equivalent" instead of saponification "value."

[4] Van der Driessen Mareeuw, *Nederl. Tijdschr. Pharm. Chemie en Toxicologie*, 1900 (12), 245; *Pharm. Weekblad*, 1905, No. 46, 948.

indigenous to the West Indies. Probably the commercial fat is also obtained from one or two other species of *Attalea*, viz., *A. excelsa*, Mart. (*Maximiliana maripa*, Drude) and *A. spectabilis*. The fat is prepared by expression or, in a cruder fashion, by boiling the fruit with water, when the fat rises to the top and is skimmed off. The expressed fat is colourless or faintly yellow; it has a mild taste and a faint, not unpleasant odour.

Maripa fat is used as an edible fat in the West Indies and French Guiana; it is also used in pharmacy.

Physical and Chemical Characteristics of Maripa Fat

Specific Gravity. At 100° C. (Water 15·5=1.)	Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Observer.
0·8686	24-25	26·5-27	270·5	17·35	4·45	v. d. Driessen Mareeuw
		23	259·5	9·49	...	Bassière[1]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Specific Gravity. At 100° C. (Water 15·5=1.)	Solidifying Point. °C.	Melting Point. °C.	Iodine Value.	Observer.
88·88	0·823	25	27·5-28·5	17[2]	v. d. Driessen Mareeuw

(*e*) AOUARA KERNEL OIL

French—*Huile d'amande d'aouara.* German—*Aouarakernöl.*
Italian—*Olio di noci di aouara.*

This oil is obtained from the kernels of the aouara palm fruit (p. 438). The kernels yield 46 per cent of a whitish solid fat of pleasant odour. The natives prepare the fat by pounding the kernels and boiling the mass with water; the skimmed-off fat is known to the natives under the name "quioquio" or "thiothio." The fat prepared by *E. Bontoux*[3] from the kernels had the acid value 9·6. The following characteristics were ascertained by him :—

[1] *Journ. Soc. Chem. Ind.* 1903, 1137.

[2] Private communication from v. d. Driessen-Mareeuw.

[3] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires*, vol. ii. 1104.

Solidifying point	26·2° C.
Melting point	29-30° C.
Saponification value	242·5-243·3
Iodine value	10·4-11·2
Insoluble fatty acids + unsaponifiable	91·7 per cent.
Neutralisation value of fatty acids	248·4-249·8
Mean molecular weight ,,	225

In Guiana "quioquio" fat is used for medicinal and edible purposes.

(*f*) PALM KERNEL OIL, PALM NUT OIL

French—*Huile de palmiste.* German—*Palmkernöl, Kernöl.*
Italian—*Sego di noce di palma.*

For tables of characteristics see p. 505.

Palm kernel oil is obtained from the kernels of the palm tree fruit (p. 439). The kernels are collected by the natives after the palm oil has been recovered from the fleshy part of the fruit; the shells are removed by the natives by cracking each nut separately with a stone or hammer. This work is chiefly done by women and children. Owing to the laboriousness of this process, and also owing to the facts that no more than about fifteen pounds of kernels are obtained by one worker in a day, and that the kernels have to be carried to the market, enormous quantities of palm nuts are wasted.[1] The kernels are collected at the coast stations and shipped to Europe. The chief receiving ports are Hamburg, Liverpool, and Marseilles.

The first palm kernels that came to Europe were brought to Marseilles as ships' ballast from the French West African colonies early in the 'fifties of the last century, and were thrown into the sea as soon as the ship was again to be loaded. An enterprising oil miller in Marseilles recognised the value of the kernels, and commenced the manufacture of palm kernel oil.

Recently several machines have been constructed for the breaking of the kernels on the spot, but in view of the exceedingly cheap labour (of women and children) in West Africa, it is doubtful whether the machines will meet with extended application in the near future. One of these was tested at the Government Botanic Gardens, Aburi, and it was ascertained that by using it the cost of labour was reduced by about 42 per cent. But, at the same time, over 20 per cent of the nuts passed through the machine unbroken. *Haake's* machine has been also tried (see "Palm Oil," p. 440), but, according to reliable information given to the author, it has not proved successful. The problem of expeditiously cracking the nuts in Africa is, therefore, still an unsolved problem, which must approach its solution in the future, as the opening up of the country by railway lines, and the increased facilities of transport by water, will assist in emphasising

[1] Nut-cracking machines have been made by *Miller* and by *Haake*, but hitherto they have not been able to supplant manual labour.

the enormous waste that is being incurred at present. It has also been attempted to express palm kernel oil on the spot,[1] but the presses were too heavy to be worked by women and children, and, therefore, fell into disuse. In this connection the author may state that it would hardly pay under present circumstances to extract the oil on the spot, as the residual cake, forming about 50 per cent of the kernels, has a high value in Europe, whereas it would be perfectly valueless in West Africa. The quantities of palm kernels that are imported into Europe are given in the following table :—

Imports of Palm Kernels into Hamburg, Liverpool, and Marseilles

Year.	Imported into Hamburg.	Imported into Liverpool.	Imported into Marseilles.
	Tons.	Tons.	Tons.
1854	...	...	364
1855	...	...	1,144
1856	...	...	2,317
1857	...	...	2,180
1875	...	...	1,796
1880	...	...	2,760
1885	...	...	20,288
1890	...	...	28,864
1895	...	...	13,385
1896	101,537	...	19,667
1897	88,707	...	12,967
1898	101,083	...	10,953
1899	106,208	...	7,685
1900	117,987	...	8,287
1901	132,005	...	8,893
1902	160,099	32,404	8,096
1903	152,078	25,446	4,628
1904	159,118	26,500	7,514
1905	156,708	22,000	3,533
1906	151,105	25,280	3,732
1907	188,019	23,450	4,439

The chief centre of the palm kernel oil industry is Harburg (near Hamburg), whence most of the palm kernel oil used in England is shipped. The following table shows the imports of palm kernel oil :—

Palm Kernel Oil imported into Liverpool

Year.	Tons.
1900	3,892
1901	4,744
1902	15,004
1903	8,448
1904	14,438
1905	11,292
1906	7,128

[1] Cp. J. Ambleston, English patent 20,185, 1904.

At present considerable quantities of palm kernel oil are being produced in Liverpool.

The total annual production of palm kernels in the French colonies reaches about 30,000 tons per annum. The following table gives some details :—

Exports of Palm Kernels from the French Colonies

(In metric tons)

Year.	Senegal.	French Guinea.	Ivory Coast.	Dahomey.	French Congo.
1900	430	2385	3108	21,986	688
1901	733	2103	2982	24,212	611
1902	481	2894	3417	29,778	728
1903	772	2819	2840	21,685	621
1904	903	2855	3366	25,997	691
1905	903	2810	3169	17,480	667

The imports of palm kernels into Marseilles have decreased considerably during the last ten years, and at present kernels are only occasionally expressed there. This is due to the cake not finding a ready sale as cattle food in the south of France, the cocoa nut cake having almost completely ousted the palm kernel cake from that market. In fact, the small quantities of cakes that were prepared in the Marseilles market were extracted with carbon bisulphide, to recover the whole amount of oil; hence the extracted cakes had only value as manure. (At present the extraction of palm nut cake with solvents has been abandoned in Marseilles as being unremunerative. The small quantities that are made are sold as cattle food.) In Germany, on the other hand, palm kernel cakes find a ready outlet as food for young pigs.

The kernels are screened to free them from shells, stones, nails, hammerheads, are passed over magnetic separators, and then ground between rollers to a paste. The pulpy mass is either expressed in hydraulic presses or extracted with solvents. In the first process the meal must be pressed twice, on account of the large proportion of fat the kernels contain.

On a commercial scale the first expression of palm kernel meal is carried out at a temperature of 45-50° C., the second at 55-60° C. Thus 43-45 per cent of palm kernel oil are recovered.

The press cake contains 6-8 per cent of oil; its proportion of nitrogen is low (about 2·5 per cent), hence its value as cattle food or even as manure is somewhat low.

The variations of the percentage of oil in the kernels will be gathered from the following two tables. The first table, due to

Fendler,[1] refers to the varieties of palm fruits described above (p. 441).

Variety.	Oil. Per cent.	Moisture. Per cent.
De	43·7	8·2
De de bakui	49·1	6·5
Se de	49·2	5·9
Afa de	45·5	6·5
Small-fruited Lisombe	49·2	...
Large-fruited Lisombe, ripe	48·9	...
Large-fruited Lisombe, unripe	49·2	...

The numbers given in the following table, due to *Nördlinger*,[2] refer to commercial brands of palm kernels :—

Origin of Palm Kernels.	Proportion of Fat. Per cent.	Origin of Palm Kernels.	Proportion of Fat. Per cent.
Sierra Leone	48·6	Togo District, French	49·3
Island of Sherboro	46·7	Lagos	50·4
Liberia	49·4	Benin	49·8
Grand Bassa	50·2	Niger	50·5
Half Jack	50·8	Brass	52·5
Apollonia	47·2	Calabar	50·9
Dixcove	48·2	Bonny	51·0
Cape Coast Castle	50·2	Opobo	52·3
Winnebah	46·1	Cameroons	49·0
Quitta	48·4	Congo	47·4
Togo District, German	52·1	Loanda	50·9

The colour of palm kernel oil is white to pale yellow. In the fresh state the oil is neutral, and has a pleasant smell and an agreeable nutty taste. Commercial samples contain, however, notable amounts of free fatty acids. The following table gives the proportions found in various samples of palm nut oil :—

Free Fatty Acids in Palm Kernel Oil

Kind of Oil.	No. of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent.	
Expressed oil	27	3·30-17·65	Nördlinger
,, ,,	2	9·8 -11·16	Emmerling
,, ,,	6	2·6 - 6·2	Lewkowitsch
Extracted oil	10	4·17-11·42	Nördlinger
,, ,,	5	6·38- 8·69	Emmerling
,, ,,	4	3·29- 4·13	Fendler

[1] *Berichte d. d. pharm. Gesellsch.* 1903, 115.
[2] *Journ. Soc. Chem. Ind.* 1895, 585.

Emmerling[1] found the following increases in the amounts of free fatty acids in some specimens of oil kept in closed bottles for two years :—

Sample No.	Free Fatty Acid calculated as Oleic Acid.	
	Fresh Oil.	After Two Years.
	Per cent.	Per cent.
1	7·39	9·25
2	6·38	8·59
3	7·54	8·74
4	9·80	11·86

On exposure to the air for four months the amount of free fatty acids increased but little, viz. from 8·59 and 8·74 to 9·10 and 10·00 per cent respectively ; whilst the amount of volatile fatty acids, measured by the *Reichert-Meissl* value, increased after four months' exposure to the light from 5·96 and 5·41 to 6·69 and 6·38. The same samples kept in the dark showed after the same time 7·28 and 6·53 per cent respectively.

The iodine values also decreased on keeping in closed bottles, as shown in the following table :—

Sample. No.	Iodine Value.	
	Fresh Oil.	Oil kept Two Years in Closed Bottle.
1	16·23	11·28
2	16·76	10·06
3	15·37	10·56
4	15·30	11·94

Palm kernel oil dissolves completely in four volumes of absolute alcohol at 32° C. (*Milliau*[2]).

The chemical composition of palm kernel oil is not fully known.

Valenta[3] examined the mixed fatty acids. By passing a current of steam through the acids a small quantity volatilised ; the distillate consisted of *caproic* acid, and most likely also of *caprylic* acid. After drying the acids that remained behind and distilling them fractionally, at a pressure of 100 to 160 mm., six fractions were obtained, the examination of which led to the results recorded in the table :—

[1] *Landw. Versuchsstationen*, 1898, 51. [2] *Compt. rend.* 1892 (115), 517.
[3] *Zeit. f. angew. Chemie*, 1889, 335.

Fraction No.	Boiling Point.	Melting Point.	Saponif. Value.	Iodine Value.	Yield.	Saturated Fatty Acids.	Oleic Acid.	Constituents of the Fraction
	°C.	°C.			Per cent.	Per cent.	Per cent.	
1	135-190	..	..	0	4	100	0	Caprylic, capric
2	190-200	31·5	310	2·6	10	97·2	2·8	Capric, oleic
3	200-205	37·5	275	3·4	58	96·3	3·7	Lauric, capric, oleic
4	205-225	32·5	264	7·8		91·5	8·5	,, ,, ,,
5	225-245	31·5	251	16·7	15	81·7	18·5	Lauric, myristic, oleic
6	245-270	35·0	219	41·3	5	54·6	45·8	Myristic, palmitic, oleic
7	Residue	..	..	..	8	..	..	

The volatile fatty acids of a specimen of palm kernel oil having the (very high) acid value 34, *Reichert-Meissl* value 5·2, and the number for insoluble volatile acids (see "Butter Fat") 9·3, were examined by *O. Jensen*,[1] who states that *butyric* acid was absent, and that the amounts of deci-normal alkali required for caproic, caprylic, and capric acids for 5 grams of the palm kernel oil were 2·5 c.c., 1·1 c.c., and 23·0 c.c. respectively (cp. "Cocoa Nut Oil," p. 520).

The chief constituent of palm kernel oil is therefore lauric acid. From the iodine value the author calculates the proportion of olein as 12 to 20 per cent. The older statement of *Oudemans* that palm kernel oil contains 26·6 per cent of oleic acid, must be abandoned as erroneous. Palm kernel oil is very nearly related in its chemical composition to cocoa nut oil. Like the latter it is remarkable on account of its high saponification value, and the notable amount of glycerides of volatile fatty acids it contains (cp. "Cocoa Nut Oil," p. 518). It also requires, like cocoa nut oil, strong caustic soda lye for saponification, and yields a hard white soap, which is only thrown out in the "salting out" process by a large amount of salt.[2]

Palm kernel oil is largely used for soap-making. The freshest oil is employed in the manufacture of vegetable butter, like "Cocoa Nut Oil" (p. 516), and of "Chocolate Fat."

In this latter manufacture a hard fat ("*palm nut stearine*") is obtained; the liquid "*palm nut oleine*," being a by-product, is used in soap-making. A sample of palm nut oleine examined by the author had the titer test 16·8° to 17° C.

Palm nut oil is not adulterated with other fats (cp. also p. 525). The edible variety of palm nut oil is, however, used for adulterating butter fat and cacao butter (see p. 479).

[1] *Zeit. f. Unter. Nahrungs- u. Genussm.* 1905, 265.

[2] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1894, March; *Journ. Soc. Chem. Ind.* 1894, 258.

Physical and Chemical Characteristics of Palm Kernel Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 60° C.	Observer.
40 (water at 15·5=1)	0·9119	Allen	23·0[3] 24·0[4] 23·0[5]	Fendler ,, ,,	23-28 25-26 30·0[3]	Valenta Thoerner Fendler	247·6 246-250 242·4-244·1	Valenta Thoerner Lewkowitsch	10·3-17·5 13·4-13·6	Valenta Morawski and Demski	5·0 5·41-5·96	Lewkowitsch Emmerling	1·4431	Thoerner.
99 (water at 15·5=1)	0·8731	,,	24·0[6]	,,	28·5[4] 29[5] 28[6]	,, ,, ,,	247·9[1] 254·8[2] 248·8[3] 249·4[4] 250·0[5] 246·3[6]	Emmerling ,, Fendler ,, ,, ,,	13-14 15·4-16·8[7]	Thoerner Emmerling	5·85[3] 6·34[4] 6·22[5] 6·82[6]	Fendler ,, ,, ,,	Butyro-refractometer.	
									14·9[3] 16·8[4] 15·6[5] 15·4[6]	Fendler ,, ,, ,,			At 40° C. "Degrees."	Observer.
													36·5	Beckurts and Seiler

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
91·1	Lewkowitsch	Titer Test.		25-28·5 20·7	Valenta Thoerner	258-265 264 251·7	Valenta Thoerner Lewkowitsch	211 222·8	Valenta Lewkowitsch	12·07 12	Morawski and Demski Thoerner	1·4310	Thoerner
		20·0-20·5	Lewkowitsch							Liquid Acids.			
		22·5-24·5	,,										
		23·5-24·5	,,							44-48	Pick[8]		
		24·6-25·5	,,										

[1] Extracted oil. [2] Expressed oil.
[3] From De palm the oil contained 54·06 per cent free fatty acids (calculated to oleic).
[4] ,, De de bakui palm ,, ,, 55·07 ,, ,, ,, ,,
[5] ,, Se de palm ,, ,, 55·38 ,, ,, ,, ,,
[6] ,, Afa de palm ,, ,, 57·18 ,, ,, ,, ,,
[7] After keeping for two years in closed bottles these values had decreased; cp. p. 503. [8] Determined in the author's laboratory.

(*g*) COCOA NUT OIL

French—*Beurre de coco ; huile de coprah.* German—*Kokosöl ; Kokosnussöl.* Italian—*Burro di cocco.*

For tables of characteristics see pp. 522-524.

Cocoa nut oil is the fat obtained from the kernels of the cocoa nut, especially from those of the two species *Cocos nucifera*, L., and *Cocos butyracea*, L.

Cocos nucifera grows on all coasts and islands of the Tropics ; in fact, it may be considered a cosmopolitan of all tropical coast-lines in both hemispheres.

De Candolle is of the opinion that the cocoa nut tree is indigenous to the islands of the Malayan Archipelago, whence the nuts were driven by the sea currents towards the east to the Pacific Islands and the coasts of Central America, and towards the west to Ceylon and the East Coast of Africa.[1]

The fruits falling into the sea are carried by the waves into distant countries, and the seed, being well protected by the "coir" (fibres), is able to germinate on all shores (islands and even coral reefs) where the fruits may be deposited. The tree grows best in the neighbourhood of the coast and a few miles inland, at low altitudes. It will also grow far inland,[2] but there it no longer bears fruit ; nor does it bear fruit in sub-tropical climates. It forms large forests, especially on the coasts of Ceylon, Java, and the Philippines. On account of its manifold uses the tree has been cultivated early in the history of mankind, and the fruits were therefore gathered, so to speak, on a commercial scale, not only in the localities named, but also in all South Sea Islands, Madagascar, Mauritius, Ceylon, Zanzibar, the East Coast of Africa, the West Coast of Africa, the Antilles, and the coast-lines of tropical South America.

The following table contains some recent statistics[3] as to the area under cultivation. The figures are, of course, only approximate ones.

	Hectares.
Ceylon	280,000
South America	200,000
India	140,000
Straits Settlements, Philippines	120,000
Java, Sumatra	100,000
South Sea (Pacific) Islands	100,000
Cochin China	40,000
Madagascar	20,000
Commores Islands, Seychelles, Zanzibar	34,000
Antilles	40,000
West Coast of Africa	40,000

[1] Hubert, *Le Cocotier*, Paris, Dunod and Pinat, 1906.

[2] Cocoa nut trees grow at Luang-Prabang, in Indo-China, a distance of about 100 miles from the sea.

[3] Statistics for 1907, see Appendix.

Cocos butyracea is indigenous to Brazil, and yields, together with *Cocos nucifera* (and all the other species of the *cocos* family mentioned already, such as *Cocos sclerocarpa*, etc.), the chief quantities of cocoa nut fats that are consumed locally. The exported cocoa nut oil is, however, mainly derived from *Cocos nucifera*.

The cocoa nut tree flowers when about 6 or 7 years old, and begins to bear fruit fully when it has reached the age of about 8 to 10 years. It then retains its fertility up to an age of 60 years and more, and under favourable conditions (as regards soil and moisture) it even bears fruit up to the age of 100 years. The cocoa nut palm, when in full vigour, produces about sixty nuts annually. The nuts contain a fleshy endosperm built up from a milky juice rich in oil. At the period of maturity of the fruit the milky juice has disappeared almost completely, and the endosperm forms the well-known cocoa nut kernel ("cocoa nut meats"), inside which the remainder of the milky juice—cocoa nut milk—is enclosed.[1] The kernel contains from 30-40 per cent of fat, and about 50 per cent of moisture. One thousand nuts yield about 200-250 kilos. of dried kernel (containing on the average about 10 per cent of moisture), which is known under the name of copra.

Since the earliest time in the history of mankind the kernels have been used by the natives of the South Sea Islands, and especially of India, as one of their chief articles of food. The mode of preparing the oil, as practised centuries ago, would therefore hardly have differed from the primitive methods described in the foregoing pages for the preparation of other fats, such as palm oil, carapa oil, etc. Thus on many South Sea Islands the kernels were cut into small pieces and exposed in piles to the sun, when the oil would run off spontaneously. An improvement on this method consisted in converting the kernels into pulp, placing the latter in vessels perforated with holes, and exposing them to the sun, when the oil would run through the holes. The oil was then collected and carried in bamboo sticks to the market, a method which is still being practised nowadays, or has been practised up to a few years ago, in the outlying parts of the Philippines.[2] Further progress was marked by the endeavour of the natives to render their process of

[1] Recent analysis by A. Behre (*Pharm. Zentralh.* 1906, 145) of the cocoa nut milk from three Ceylon cocoa nuts gave the following results :—

Specific gravity at 15° C.	1·0244	1·0269	1·0325
100 c.c. contained—			
Water	94·20	93·55	92·25 grms.
Extract	5·797	6·447	7·746 ,,
Ash	0·665	0·802	1·000 ,,
Proteids	0·811	0·300	0·441 ,,
Fat	..	0·015	0·014 ,,
Phosphoric acid as P_2O_5	0·051	0·103	0·182 ,,
Chlorine	0·158	0·220	0·221 ,,
[α]D in 200-mm. tube before conversion	+3° 28′	+4° 12′	+5° 10′
,, ,, ,, after conversion	−1° 8′	−2° 1′	−2° 25′

Cp. also E. de Kruyff, *Bullet. du Départ. de l'Agric. aux Indes néerland.*, iv. 1907.

[2] Practically the same process is employed by the natives of Cochin China and Annam (*Bull. économ. de l'Indo-Chine*, No. 45, Sept. 1905 ; *Les Principaux Oléagineux de l'Indo-Chine*, Hanoi, 1906.

manufacture independent of the heat of the sun—as in the rainy season. Thus the kernels were laid on hurdles, formed from bamboo staves and cocoa nut leaves, and dried over a slow fire. The dried kernels were then pounded and subjected to expression in an improvised press (cp. Chap. XIII.).

In India, where cocoa nut oil became at an early date an extensively used food product, and where it not only replaced butter, but was also used for pharmaceutical purposes, more refined methods of preparation were resorted to. The nuts were split into halves by a blow with a sharp instrument, the cocoa nut milk was poured off, and the halves exposed to the sun to dry, when the kernels became readily detachable from the shell. The dried kernels were then triturated and expressed. A still better product was obtained by throwing the pounded kernels into boiling water, when the oil rose to the top, ready to be skimmed off. The residual mass was used as cattle food (*cocoa nut poonac*). This process was carried out with special care at Cochin at the coast of Malabar. It has remained in existence to the present day, and the reputation of Cochin cocoa nut oil for best quality has been maintained to this day (see below).

In carrying out the primitive processes sketched above it was found, no doubt accidentally, when owing to a good harvest a surplus of nuts was obtained, that the kernels could be preserved for some time by drying them thoroughly so as to remove the bulk of the water. The absence of a considerable quantity of moisture prevented the setting in of excessive hydrolysis and subsequent rancidity, and at the same time prevented the growth of fungi. It will therefore be readily understood that at an early stage of civilisation the production of such dried kernels (" copra ") developed into a manufacturing process.

Cocoa nut oil became first known in Europe in the eighteenth century, but did not find any commercial use till the middle of the last century, when its characteristic properties as a soap-making material were fully recognised and rapidly created a great demand for the oil. This demand has since then grown to such an extent (as will be gathered from the statistical tables given below) that almost every part of the Tropics is contributing to the supply of cocoa nut oil. And yet the production of this oil is still in its infancy, and strenuous efforts are being made, especially in the West Indies and at the West Coast of Africa, to increase the production. In commerce three qualities of oil are distinguished : (1) Cochin oil, (2) Ceylon oil, (3) Copra oil.

(1) *Cochin* oil is the finest and whitest quality. As stated already, a considerable amount of Cochin oil was prepared originally at the coast of Malabar by boiling the kernels with water and skimming off the oil. This oil owed its fine quality to the freshness of the kernels. A considerable quantity of " Cochin oil " was also made in crude native mills by expression ; during the latter years modern plant has been introduced into India such as is in vogue in Europe (see Chap. XIII.). Cochin oil, being obtained from fresh nuts, remains

for a short time only exposed to the air in contact with the putrescible matter of the kernel, and therefore contains only a very small amount of free fatty acids. The author found the percentages varying from 1·5 to 3 per cent, calculated to oleic acid. Of course, other cocoa nut oils prepared from fresh kernels with the same care are equal in this respect to Cochin oil. Hence the name "Cochin" has become a generic term for the finest quality of oil, and we therefore find in commerce the commercial brands: Cochin Cochin-China, Cochin Australia, Cochin Mauritius, Cochin South America. Cochin "neige" is a special quality of white filtered oil.

The superiority of Cochin oil to Ceylon oil seems to be due to some extent to the better climate, as the Malabar coast enjoys a larger number of dry months than does Ceylon. Hence the kernels can be dried in the sun, whereby a whiter and better flavoured oil is obtained than the Ceylon oil quality. The superiority of Cochin oil is, however, chiefly due to better cultivation of the plant (manuring, pruning, destruction of insects,[1] etc.) and better and cleanlier methods of manufacture. The Cochin oil is also stated to contain a larger amount of "stearine" than the Ceylon oil. But this appears doubtful, and may be due to the larger yield of "stearine" obtainable on a large scale, owing to Cochin oil containing a smaller amount of free acids than do Ceylon oils.

By expressing the kernels in the cold an oil of the solidifying point 13°-12° C., and the melting point 20° C. is obtained. This cold-pressed oil, however, is not a commercial product, being used on the spot as a substitute for butter fat.

(2) *Ceylon* oil is prepared in a similar manner (*i.e.* either by boiling or by expressing) in the plantations of Ceylon. This oil, no doubt owing to a certain want of care on the part of the natives as compared with that exercised by the natives of the Malabar coast, represents a second quality of cocoa nut oil. Ceylon oil contains a higher percentage of free fatty acids than Cochin oil. The author found in the examination of a large number of samples, extending over a series of years, from 5-10 per cent of free fatty acids (as oleic). Owing to the changes which the putrescible substances of the kernels have undergone before expression, Ceylon oil possesses the peculiar acrid taste which a cocoa nut oil of a somewhat pronounced rancid character has acquired. This drawback seems to be gradually disappearing, as, according to private information supplied to the author, there are at present some establishments in Ceylon in which cocoa nut oil is prepared by modern methods, so that it approaches Cochin oil in freshness and low percentage of free fatty acids. The "poonac" is consequently of the same good quality as the Malabar "poonac," and considerable quantities are even exported. The extent to which the cocoa nut oil industry has grown in Ceylon

[1] In the East the cocoa nut beetle is now becoming one of the greatest pests of the cocoa nut palm. The ravages effected by this beetle in Rangoon are such that the total disappearance of the tree is feared. In Ceylon, special regulations are in force to prevent the spreading of this pest.

may be gathered from the following tables, giving the values[1] in rupees, and quantities of the exports of some of the cocoa nut products from Ceylon (cp. also table below, Exports of Copra):—

Exports of Cocoa Nut Palm Products from Ceylon (Values)

	1901.	1902.	1903.
	Rupees.	Rupees.	Rupees.
Cocoa nuts	773,391	711,918	649,635
Cocoa nuts desiccated	2,314,708	2,870,549	3,104,689
Coir fibre	700,603	778,174	793,134
Coir manufactured	10,561	11,559	9,575
Coir and rope	137,462	165,560	207,670
Coir yarn	854,538	799,785	945,357
Copra	4,540,693	4,098,947	7,531,540
Cocoa nut oil	7,601,233	10,007,860	11,022,596
Cocoa nut shells	27,060	32,623	51,993
Poonac (oil cake)	937,474	1,283,264	1,499,820

Exports of Cocoa Nut Palm Products from Ceylon (Quantities)

	1904.	1905.	1906.
Cocoa nut oil (cwts.)	499,632	594,821	539,070
Copra (cwts.)	714,295	393,309	451,134
Cocoa nut desiccated (lbs.)	18,728,915	20,779,236	20,213,570
Poonac (cwts.)	245,789	270,703	259,125
Cocoa nuts (number)	16,957,621	18,047,718	16,013,510
Coir rope (cwts.)	21,832	21,468	20,643
Coir yarn (cwts.)	90,722	113,063	102,993
Coir fibre (cwts.)	126,793	150,920	164,928

A further classification of the quantities of cocoa nut oil shipped from Ceylon during recent years is given in the following table:—

Shipments of Ceylon Oil

Country.	1904.	1905.	1906.
	Tons.	Tons.	Tons.
England	10,491	15,992	9,313
America	5,073	5,587	4,896
Other countries	5,473	8,162	12,744
Total	21,037	29,741	26,953

(3) *Copra* oil is prepared in modern factories in Europe, the United States, and in Australia[2] from copra (*i.e.* the dried kernels), which is

[1] *Bull. Imp. Inst.* 1905, 3, 217.

[2] The northern coasts are now being planted with cocoa nut palms.

imported in enormous quantities into these countries. The conversion of the kernel into "copra" is not only a convenient method for reducing the cost of freight, but is pre-eminently a cheap process for preserving the cocoa nut oil as far as possible. The earliest process of manufacturing copra consists, as has been pointed out above, in exposing the broken kernel in smaller or larger pieces to the sun, when most of the moisture evaporates. Copra so prepared is sold as "sun-dried" copra. The sun-dried copra is of much better quality than the kiln-dried (see below), for it gives a light-coloured cocoa nut oil having only a slight yellow tinge, which can be readily removed by treating the oil with char in the course of refining. A more rapid process of obtaining copra is to dry it in kilns by the aid of fire. The primitive method in which these kilns (originally nothing else but grills consisting of a bamboo grating on which the split nuts were placed face downwards) were erected and managed, gave the fumes ready access to the copra itself, so that even the best kiln-dried copra was characterised by a peculiar empyreumatic smell. Inferior copra was partly roasted or even burnt at the outside. Such copra gives a yellowish oil which proves refractory in the bleaching process. At present, improved methods of drying copra in kilns are being introduced. In India, as also in some of the Pacific Islands, drying by hot air is being resorted to. The best practice is to bring the nuts, immediately after they have been picked up, into sheds, so as to protect the kernels against the influence of sun or rain, as the case may be. Then the fibres ("coir") are removed, the nuts split open, the kernels cut into small pieces, and the "meats" placed on hurdles (consisting of bamboo sticks and cocoa nut leaves arranged on small waggons), which are drawn slowly through a heated tunnel in which the copra is meeting hot air on the counter-current principle. The copra prepared by this process is, up till now, chiefly used in confectionery, and fetches a higher price than sun-dried copra.

In the British West Indies drying by means of hot air in a rotary dryer has been introduced, and the results are considered very satisfactory, as thereby the best copra on the market is obtained. Similar plant is being introduced in the Samoa Islands.

It would appear that drying *in vacuo* would be a still more preferable method. Although *H. S. Walker*,[1] who has carried out experiments on a small scale with a vacuum apparatus, states that this method does not yield satisfactory results, no definite conclusion should be drawn from these experiments; for they were carried out on too small a scale, and the kernels were exposed for too long a time to an elevated temperature. In the author's opinion, a process which combines the rotary dryer with the application of vacuum should yield satisfactory results.[2]

Whereas the fresh kernels contain about 30-40 per cent of fat, the sun-dried copra contains as much as 50 per cent. In kiln-dried

[1] *The Philippine Journ. of Science*, vol. i. p. 118.

[2] Cp. Lewkowitsch, "Evaporation *in vacuo*," *Journ. Soc. Chem. Ind.* 1905, 11, 49.

copra the percentage of fat rises to 63 per cent and even 65 per cent. In hot-air-dried copra the percentage of fat reaches even 74 per cent. If the copra is properly dried so that the percentage of water falls to about 4 per cent, fungi do not develop on it, and the fat will consequently undergo little change during transport (in bags) on board ship. Copra as now made retains, however, mostly 9 or 10 per cent of water, a proportion which favours the growth of fungi. Hence such copra is easily attacked by them, with the consequent deterioration of the oil (see Vol. I. Chap. I.), and the formation of free fatty acids.

The following table, due to *Schindler* and *Waschata*,[1] states in detail the percentages of fat obtained in the examination of some kiln-dried and hot-air-dried copras :—

No.	Origin.	Year.	Water.	Fat.
1	Ceylon	1900	...	71·40
2	,,	1900	...	67·36
3	,,	1901	3·65	69·17
4	Penang	1900	...	68·95
5	,,	1900	...	67·08
6	Sangir	1900	...	68·93
7	Malabar	1900	...	71·03
8	Singapore	1900	...	69·05
9	,,	1900	...	65·91
10	Java	1900	...	68·77
11	,,	1900	...	67·06
12	,,	1902	...	66·21
13	Pontianak	1900	...	65·43
14	Manila	1900	4·61	64·47
15	,, (special quality)	1900	...	67·55
16	,,	1901	...	67·10
17	,,	1901	...	68·57
18	,,	1902	...	68·34
19	Pacific Islands	1900	4·10	74·72
20	Zanzibar	1901	...	70·23
21	Tangiers	1903	...	67·00
	Means of twenty-one analyses			68·30
	Maximum			74·72
	Minimum			64·47

In the following table an attempt is made to classify the different copras on the market in the order of their quality, commencing with the best. It should, however, be noted that the order is subject to great fluctuations, and must vary from year to year :—

Kind of Copra.	Mode of Drying.
Malabar	Sun-dried
Seychelles	,,
Venezuela (Caracas, Porto Cabello)	,,
Ceylon	,,

[1] *Chem. Revue*, 1905, 169.

Kind of Copra.	Mode of Drying.
Java	Sun-dried
Cébu (Dutch Indies)	,,
Mozambique	,,
Nouméa (New Caledonia)	,,
Dahomey (Quittah)	,,
Celebes	,,
Borneo	,,
Sumatra	,,
Macassar	Kiln-dried
Manila	,,
Zanzibar	Sun-dried
Saigon	,,
Pacific Islands	,,

The copra is treated in the oil mills in a similar manner to that in which palm kernels (see p. 501) are worked up. The meal is expressed twice at a temperature of 55-60° C.; the practical yield of oil varies from 63 to 66 per cent according to the content of oil in the raw material. The expressed oil contains, according to the quality of the copra, more or less of free fatty acids.

The author found in a large number of copra oils up to 25 per cent of free fatty acids (see p. 502, "Palm Kernel Oil," and Chap. XIII.).

The oils high in content of free fatty acids are sold for soap-making purposes after a preliminary boiling up with water and filtration. Only the most carefully prepared copra will yield an oil that can be used for edible purposes (cp. Chap. XV. "Vegetable Butters").

The cocoa nut cakes contain from 7 to 10 per cent of fat, but are low in percentage of proteins (about 20 per cent) as compared, *e.g.*, with sesamé cakes. Nevertheless the cocoa nut cakes form a valuable food for dairy cattle; they are said to increase the well-being of milch cows and to stimulate the secretion of milk.[1]

It should, however, be stated that *Einecke*[2] demonstrated by experiments that cocoa nut cake has rather a depressing than a stimulating action as regards the quantity of fat in the milk, and that therefore the influence of cocoa nut cake on milk-fat production should be judged as being *nil*.

Trials have been made to extract the cocoa nut oil from copra by solvents, but all attempts have been abandoned owing to the unremunerativeness of the process (cp. Chap. XIII. p. 25). Only under exceptional market conditions, such as the extremely high prices ruling in 1907 for cocoa nut oil, does it pay to extract the oil from the cake by means of solvents, and to sell the residue for manuring the land.

[1] Cp. Garola, *Contribution à l'étude des tourteaux alimentaires*, Chartres, 1892; cf. also Collin and Perrot, *Les Résidus industriels utilisés par l'agriculture comme aliments et comme engrais*, Paris, 1904.

[2] *Mitt. des landw. Instit. d. Univ.*, Breslau, 1903, 2, 559.

The amounts of copra coming into the world's markets may be gathered from the following table :—

Exports of Copra

From	1904.	1905.	1906.
	Tons.	Tons.	Tons.
Java	...	107,709	49,160
Straits (Singapore, Penang)	...	58,915	36,255
Manila	...	52,520	57,135
South Sea (Pacific) Islands[1] (approximately)	...	30,000	...
Macassar	...	25,961	9,041
Sangar	...	19,514	...
Ceylon	31,768	17,739	20,697
Zanzibar	...	10,000	...
Mozambique	...	5,000	...
Padang	...	6,580	...
Other places of origin—such as Indo-China, Réunion, Seychelles, Mauritius, French Guyana, German East and West Africa (Togo, Cameroons, etc.)	...	20,000	...

From the numbers given, the great variation in the production will become at once apparent. (The shortage in the production of 1906 found its commercial expression in the very high prices of cocoa nut oil during 1907.) Almost the total quantity of Ceylon copra went to Germany, Austria, France, and Belgium.

In view of the importance which Marseilles has gained as a centre of the cocoa nut oil industry, the following tables will be found useful :—

Imports into Marseilles of Copra and Cocoa Nut Oil

Year.	Copra.	Cocoa Nut Oil.
	Kilogrammes.	Kilogrammes.
1846	1,370,000	...
1857	960,000	...
1875	712,000	1,076,560
1880	852,900	4,282,895
1885	22,092,943	2,435,402
1890	34,163,594	437
1895	70,957,593	18,241
1900	104,207,947	10,679
1905	110,352,751	1,233,308

[1] Samoa sends to the Australian market alone about 4000 tons per annum. In 1903 the total quantity shipped from Western Samoa was 7000 tons. The total production at present is about 8600 tons, of which nearly two-thirds is supplied by the natives, whereas the remainder is expressed in the plantations of the Deutsche Handels- und Plantagen Gesellschaft. About 5000 tons were sun-dried, the remainder hot-air-dried copra. German New Guinea produces over 1000 tons per annum, the Carolines and the Palau and Marianen Islands over 2000 per annum, and the Marshall Islands over 2200 tons per annum.

Exports from Marseilles of Cocoa Nut Oil (or Copra [1]) :—

Year.	Tons.
1870	40
1875	106
1880	922
1885	2,303
1890	9,437
1895	7,610
1900	10,234
1905	10,776

The quantities of copra imported into France, Marseilles, and Hamburg are placed side by side in the following table :—

Year.	France.	Marseilles.	Hamburg.
1896	81,378	75,206	21,084
1897	68,074	63,032	10,791
1898	69,453	63,398	14,096
1899	83,069	74,094	11,523
1900	106,101	94,360	21,034
1901	81,069	74,626	19,983
1902	91,953	85,382	43,522
1903	104,316	95,459	48,652
1904	88,111	81,126	48,586
1905	110,578	102,975	88,165
1906	102,984	97,720	79,942
1907	97,277	94,292	

The following table gives a synopsis of the cocoa nut oil trade of the United Kingdom. The figures given above for the shipments of cocoa nut oil from Ceylon are, of course, included :—

Imports of Cocoa Nut Oil into, Exports from, the United Kingdom, and Home Consumption

Year.	Imports of Cocoa Nut Oil.	Exports of Cocoa Nut Oil.	Sold for Home Consumption.
	Tons.	Tons.	Tons.
1897	12,137	3,568	8,569
1898	15,355	3,350	12,005
1899	22,915	5,299	17,616
1900	27,637	7,040	20,597
1901	23,908	8,138	15,770
1902	24,793	7,334	17,459
1903	39,132	11,075	28,057
1904	30,762	11,330	19,432
1905	30,658	12,860	17,798
1906	26,902	9,152	17,750

[1] The exported copra is chiefly shipped to the United States.

In the year 1907 the value of the imports, exports, and home consumption amounted respectively to £857,879, £424,860, and £433,019.

Cocoa nut oil is, in our climate, at the ordinary temperature a solid white fat. It has a bland taste, and, in its fresh state, the peculiar though not unpleasant odour of cocoa nuts. The opinion generally accepted up to a short time ago that cocoa nut oil easily turns rancid must be now considered as erroneous. This opinion was due to the fact that the cocoa nut oils imported, as also the cocoa nut oil made from the copra as shipped up to a few years ago, generally contained not only free fatty acids but also products of rancidity (following in the wake of the formation of free fatty acids) which imparted to the cocoa nut oil its peculiar, objectionable taste. Even after the free fatty acids were removed, some impurities [no doubt secondary products, formed by the action of fungi (cp. Chap. I.), or enzymes on the putrescible matter of the kernels] still remained in the fat, causing it to become more or less hydrolysed and subsequently rancid on keeping. If the oil is prepared from fresh kernels by boiling (as is done on the Malabar coast and to some extent in Ceylon), or even if the oil is prepared from carefully selected and well-dried copra, the fat undergoes very little change and only shows a slight proportion of free fatty acid, but not yet those objectionable products of rancidity, which cannot be removed by any practical process of refining. It is, therefore, possible at present to prepare edible cocoa nut oil which behaves as regards keeping quality like any other oil or fat. The best edible cocoa nut oils on the market represent a practically neutral cocoa nut oil (cp. Chap. XV. "Vegetable Butters").

In the preparation of the best brands of vegetable butters the free fatty acids and malodorous substances are removed. Some makers also take out a portion of the liquid glycerides by expression in hydraulic presses. In the manufacture of "cocoa nut stearine" the removal of the liquid glycerides ("cocoa nut oleine") is carried so far that 50 to 80 per cent are expressed, according to the desired melting point of the solid product. For the latter the author has proposed the name "Chocolate fat" (cp. Chap. XVI.). In the same manner a technical "cocoa nut stearine" is prepared (from copra oils of ordinary quality) which is used in the manufacture of composite candles and night-lights (cp. Chap. XVI.). The "cocoa nut oleine" is worked up for soap.

The following numbers have been ascertained in my laboratory by *Clapham*, *Calderwood*, and by the author for commercially prepared samples of cocoa nut oleine, cocoa nut stearine, and chocolate fats :—

[TABLE

Fat [1]

Cocoa Nut.	Specific Gravity.			Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
	At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
"Oleine"	60	0·92931	Clapham	265·35	Calderwood	14·8	Calderwood	7·95	Calderwood
"Stearine"				255·63	,,	4·0	,,	4·45	,,
				251·5	Lewkowitsch	5·2	Lewkowitsch	3·85	Lewkowitsch
								6·34	,,
				254·3	,,	6·64	,,	3·24-4·89	,,

Fatty Acids

Cocoa Nut.	Insoluble Acids + Unsaponifiable.		Titer Test.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
	Per cent.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Liquid Fatty Acids.	
"Oleine"	85·25	Clapham	20·6 [2]	Calderwood	267	Clapham	210·0	Clapham	36·3	Clapham
			20·1 [3]	,,	266·9	,,	210·2	,,		
			20·6	Clapham			204·6	Calderwood		
"Stearine"			26·55 [2]	Calderwood						
			26·42 [3]	,,			211·4	,,		

[1] Determined in the author's laboratory. [2] Fatty acids washed with water. [3] Fatty acids washed with brine.

The quantity of edible cocoa nut oil (including edible palm kernel oil) produced a few years ago in Europe alone, amounted to about 10,000 tons per annum,[1] and rose rapidly to 50,000 tons. The remunerativeness of this manufacture led to an over-production and the flooding of the market with inferior qualities (cp. Chap. XV. "Vegetable Butter").

Neutral cocoa nut oil dissolves completely in two volumes of absolute alcohol at 32° C. (*Milliau*[2]). One volume of cocoa nut oil dissolves also in two volumes of 90 per cent alcohol at 60° C. As to the characteristic crystalline form of cocoa nut oil crystals under the microscope see "Butter Fat."

Cocoa nut oil resembles palm nut oil in its chemical composition; like the latter it contains large proportions of trimyristin and trilaurin, smaller quantities of tripalmitin,[3] tristearin, and triolein, as also the glycerides of the volatile acids caproic, caprylic, and capric. It is practically free from hydroxy acids[4] (*Lewkowitsch*), and free from butyric acid.

The occurrence of tristearin is recorded here, as a specimen of commercial cocoa nut oil examined in the author's laboratory yielded 0·99 per cent of stearic acid.

Ulzer[5] doubted the occurrence of palmitin in cocoa nut oil, as he could not detect any palmitic acid. In view of the fact that *Oudemans* did identify palmitic acid, and of the further fact that the presence of stearic acid had been proved by the author, this statement stood in need of confirmation. *J. J. Reijst*[6] lately averred that stearin did not occur in cocoa nut oil. The statements of *Ulzer* and *Reijst* have recently been shown to be erroneous by *Haller* and *Youssoufian*,[7] who have proved, in an exhaustive examination of the fatty acids obtained by fractionation of the methylesters (Chap. XII.), that both palmitin and stearin occur in cocoa nut oil. These chemists confirm the occurrence of caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic acids, all of which have been identified by their methylesters. They could not detect butyric acid, the absence of which from cocoa nut oil had already been recognised by *A. Kirschner* and by *O. Jensen* (cp. below).

Tolman and *Munson* obtained, by the lead-salt-ether method, 65·9 per cent of solid acids; this agrees satisfactorily with a later statement of *Lane*,[8] who obtained from cocoa nut oil, by treating the lead salts with both cold and hot ether, 34·5 and 37·5 per cent of liquid fatty acids respectively. Of course, the liquid acids must not be taken in this case to represent oleic acid, as the iodine value of cocoa nut oil does not allow for so high a percentage of this unsaturated acid. Indeed, the proportions of the liquid acids were found by *Lane*

[1] Lewkowitsch, *Cantor Lectures on Oils and Fats: their Uses and Applications*, 1904, p. 22.

[2] *Compt. rend.* 1892, **115**, 517.

[3] Oudeman's *Journ. f. prakt. Chem.* 81 (1860), 375.

[4] Unpublished experiments. [5] *Chem. Revue*, 1899, 203.

[6] *Rec. des trav. des chim. des Pays-bas*, xxv. (1906), 271.

[7] *Compt. rend.* 1906, **143**, 803. [8] *Journ. Soc. Chem. Ind.* 1904, 1104.

to amount to 22·17 and 19·52 per cent respectively. It is evident that glycerides of the volatile acids had passed into the ethereal solution of the lead salts.

The amount of total volatile fatty acids found in the author's laboratory in the examination of a number of cocoa nut oils has been given above (Chap. VIII.). Tested by *Polenske's* method (see below) the author obtained, with a number of edible cocoa nut oils, the *Reichert-Meissl* values (*i.e.* soluble volatile acids by *Reichert-Meissl's* method) 7·3-7·5, whereas the insoluble volatile acids (for 5 grams) required from 15·5-20·5 c.c. of decinormal alkali. (The numbers which *Polenske* gives for the latter, viz. 16·8-17·8, having been derived from too small a number of observations must, therefore, be corrected.) *Müntz* and *Coudon* found in four edible cocoa nut oils from 2·26 per cent to 2·70 per cent of total volatile acids calculated to butyric acid (as determined by the French official method, see Vol. I. Chap. VIII.), and from 8·89 per cent to 10·06 per cent of total insoluble volatile acids (also expressed in terms of butyric acid). Since the highest and lowest values for the soluble volatile and insoluble volatile acids are not in strict correspondence, the figures are given in detail in the following table :—

Edible Cocoa Nut Oil.	Volatile Soluble Acids in terms of Butyric Acid.	Insoluble Volatile Acids in terms of Butyric Acid.
No.	Per cent.	Per cent.
1	2·51	9·63
2	2·49	10·06
3	2·26	9·76
4	2·70	8·89

The same edible cocoa nut oils, examined by *Müntz* and *Coudon's* method (see below), gave the following figures :—

Edible Cocoa Nut Oil.	Soluble Volatile Acids in terms of Butyric Acid.	Insoluble Volatile Acids in terms of Butyric Acid.	Relation :— $\frac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100$.
No.	Per cent.	Per cent.	
1	1·20	3·01	250·3
2	1·23	3·38	274·4
3	1·15	3·63	314·7
4	1·27	3·60	282·3

It should of course be noticed that these numbers refer only to the special brands of edible cocoa nut oil examined, and do not apply generally to all kinds of cocoa nut oil.

Segin, who attempted to determine separately the molecular weights of the total volatile acids, of the soluble volatile acids, and of the insoluble volatile acids, found the following numbers respectively :— 114, 163, 156. These figures agree satisfactorily, as regards the

insoluble volatile acids, with a figure which the author has derived as the mean of a number of experiments, viz. 161. *Kirschner* could not detect butyric acid amongst the volatile acids of cocoa nut oil; he found that caproic acid is only present in small quantities, and that the bulk of these fatty acids consists of caprylic acid. *O. Jensen* confirms the absence of butyric acid, and gives as the numbers of decinormal KOH required for the neutralisation of the volatile acids from 5 grams of a specimen of cocoa nut oil (of the acid value 0, *Reichert-Meissl* value 6·8, and insoluble volatile acid number 13·0 by *Polenske's* method) the following amounts of alkali: for caproic acid 21·4 c.c., caprylic acid 20·5 c.c., capric 31·2 c.c. It will be seen that the statements of the two observers do not agree.

Paulmyer [1] resolved the fatty acids of cocoa nut oil, by fractional distillation in a current of steam, into ten equally large fractions. The neutralisation values and mean molecular weights of the several fractions were determined with the following result:—

	Neutralisation Value.	Molecular Weight.	Corresponding to
1st Fraction	329·4	170	0·25 per cent Caproic Acid, $C_6H_{12}O_2$ 0·25 ,, Caprylic ,, $C_8H_{16}O_2$ 9·50 ,, Capric ,, $C_{10}H_{20}O_2$
2nd ,,	310·8	180	10 ,, Capric ,, $C_{10}H_{20}O_2$
3rd ,,	292·8	191	
4th ,,	281·6	199	20 ,, Lauric ,, $C_{12}H_{24}O_2$
5th ,,	276·0	203	20 ,, Lauric ,, $C_{12}H_{24}O_2$
6th ,,	268·2	209	
7th ,,	261·4	214	10 ,, Myristic ,, $C_{14}H_{28}O_2$
8th ,,	245·7	228	10 ,, Myristic ,, $C_{14}H_{28}O_2$
9th ,,	230·0	244	4 ,, Myristic ,, $C_{14}H_{28}O_2$ 6 ,, Palmitic ,, $C_{16}H_{32}O_2$
10th ,,	207·6	270	4·6 ,, Palmitic ,, $C_{16}H_{32}O_2$ 5·4 ,, Oleic ,, $C_{18}H_{24}O_2$

According to this examination the total fatty acids of cocoa nut oil would seem to consist of—

0·25	per cent	caproic acid.
0·25	,,	caprylic ,,
19·50	,,	capric ,,
40·0	,,	lauric ,,
24·0	,,	myristic ,,
10·6	,,	palmitic ,,
5·4	,,	oleic ,,

It should, however, be borne in mind that notable quantities of caproic and caprylic acids must have been lost, and that the proportion of these two acids must be somewhat higher. It would further appear that the amount of oleic acid is too low.

[1] *La Savonnerie marseillaise*, 1907, No. 78.

The proportion of unsaponifiable matter in cocoa nut oil is small. The author obtained from a large number of cocoa nut oils examined by him amounts of unsaponifiable matter, varying from 0·179 per cent to 0·297 per cent.[1] The phytosteryl acetate prepared from the unsaponifiable matter melted at 129·5° C. *Siegfeld*[2] found in an edible cocoa nut oil 0·17 per cent of unsaponifiable matter, from which he prepared a phytosterol which melted, after the sixth crystallisation, at 140·8° to 141·8° C. The melting point of the acetate, after the seventh crystallisation, was 128·3° to 129·3° C. From another specimen of cocoa nut oil *Siegfeld* obtained 0·184 per cent of unsaponifiable matter, from which he isolated a phytosterol which melted, after the seventh crystallisation, at 140·7° to 141·7° C. The melting point of the acetate after the seventh crystallisation was 129° to 130° C.

König and *Schluckebier*[3] found in the fat extracted from cocoa nut *cake* 0·56 per cent of unsaponifiable matter, which consisted almost entirely of phytosterol, melting at 137° C.

H. Matthes and *E. Ackermann*[4] state (in a preliminary communication) that the unsaponifiable matter of a specimen of cocoa nut oil examined by them consisted of 0·125 per cent of crude phytosterol, melting at 135-140° C., and of 0·025 per cent of a liquid substance. The acetylated crude phytosterol melting from 126° - 128° C. yielded, on brominating in a solution of ether and glacial acetic acid, thin crystals of a bromide melting from 180° - 183° C. From the filtrate there were obtained, after boiling down and recrystallising from alcohol, micro-crystalline aggregates melting at 132-135° C., which is the melting point of the di-bromide of phytosterol acetate.

The "titer test" of the fatty acids of cocoa nut oil varies according to the amount of washing given to the fatty acids in the course of their preparation. Thus a sample of cocoa nut oil, the fatty acids of which were washed as described in Vol. I. Chap. III., had the titer test of 22° C., whereas by washing with brine, in which the volatile fatty acids are less soluble than in water, a titer test of 21° C. was obtained. The respective mean molecular weights, calculated from the neutralisation values 261·4 and 267·7, were in the same order, 214·6 and 209·5.

In the valuation of cocoa nut oil for soap-making, due regard must therefore be paid to the manner in which the fatty acids are prepared for the titer test.

Cocoa nut oil is used in enormous quantities in the manufacture of soaps, made by the boiling process as also by the cold process. It is also used extensively as a vegetable butter and as a chocolate fat (see Vol. III. Chap. XV.). Its use for batching jute after it has been boiled with caustic alkali has been patented.[5]

[1] With regard to the proteins in cocoa nut oil cp. Chap. XV. "Vegetable Butters."

[2] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1904, 581.

[3] *Ibid.* 1908, xv. 642.

[4] *Berichte*, 1908, 2000.

[5] German patent 184,736.

Physical and Chemical Characteristics of Cocoa Nut Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15·5	0·9259	Tolman and Munson	19·5-15·7	Valenta	23·5-24·1	Valenta	257·3-268·4	Valenta	8·9	Hübl
			16-14	De Negri and Fabris	26·2-26·4	Filsinger	250·3	Moore	9-9·5	Thoerner
18	0·9250	Stilurell			24-27	De Negri and Fabris	washed oil		9-10	Lewkowitsch
37·8	0·910-	Moore					246·2	,,	8·54 [1]	Crossley and Le Sueur
(=100° F.)	·9167		20-16	,,	23-26	,,	253·4-262	De Negri and Fabris	8·41 [2]	,,
(water at 37·8=1)			22-23	Thoerner	23·5-25	Crossley and Le Sueur			8·25 [3]	,,
40	0·9115	Allen					255-260	Thoerner	8·74 [4]	Wijs
(water at 15·5=1)							258·2 [1]	Crossley and Le Sueur	8·39 [5]	,,
99	0·8736	,,							8·84 [6]	,,
(water at 15·5=1)							255·6 [2]	,,	9·32 [7]	,,
100	0·9030 [1]	Crossley and Le Sueur					255·5 [3]	,,	8·0	Lane
(water at 100=1)							251-261	Lewkowitsch		
	0·9040 [2]	,,								
	0·9042 [3]	,,								

[1] Malabar oil. [2] Bengal oil. [3] Bombay oil. [4] "Cochin neige."
[5] "Cochin prima." [6] Ceylon oil. [7] "Ceylon prima."

Physical and Chemical Characteristics of Cocoa Nut Oil—continued

Reichert Value.		Refractive Index.			Viscosity.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 60° C.		Observer.	Seconds at 140° F.	Observer.
3·7	Reichert	1·441		Thoerner	63·9 [1]	Crossley and Le Sueur
3·5-3·7	Allen, Moore, Muter	Butyro-refractometer.			64·7 [2]	,,
					64·5 [3]	,,
Reichert-Meissl Value.		At °C.	"Degrees."	Observer.		
7·0	Lewkowitsch	15·5	49·1	Tolman and Munson		
7·5	Thoerner					
6·71 [1]	Crossley and Le Sueur	40	33·5	Beckurts and Seiler		
6·79 [2]	,,	,,	35·5	Mansfeld		
6·65 [3]	,,	,,	34·2	Crossley and Le Sueur		
8·4 [4]	Ulzer					

[1] Malabar oil. [2] Bengal oil. [3] Bombay oil.

[4] In view of the figures given by O. Jensen the correctness of this high number is open to doubt.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At 98°-99° C. (water at 15·5=1).	Observer.	° C	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
88·6-90·5	Lewkowitsch	0·8354	Allen	20·4	Hübl	24·6	Hübl	258	Thoerner	196-204	Alder Wright	8·39-8·79	Morawski and Demski	1·4295	Thoerner
82·4 [1]	Crossley and Le Sueur			19·5-15·7	Valenta	24-25	Valenta			201	Williams	9·3	Williams		
				18-16	De Negri and Fabris	25-27	De Negri and Fabris			211 [3]	Lewkowitsch	8·62-8·92	De Negri and Fabris		
85·25 [2]	Clapham			20	Thoerner	24-25	Thoerner					8·5-9	Thoerner		
				Titer Test.								Iodine Value of the Liquid Fatty Acids.			
				21·2-22·55	Lewkowitsch							36·3 [2]	Clapham		
				21·9-24·7	,,							31·9	Tolman and Munson		
				23·0-23·6	,,										
				23·3-23·9	,,							22·2	Lane		
				23·9-25·0	,,										
				24·8-25·2 (Cochin)	,,										

[1] Bengal oil. [2] Determined in the author's laboratory in a sample of commercial "cocoa nut oleine" (see p. 517). [3] Ceylon oil.

Cocoa nut oil is not adulterated with other fats; at any rate this holds good for the oil imported into England. Nevertheless, if the prices are high (as was the case in 1907), the inducement to adulterate cocoa nut oil may present itself. *Milliau* states that cocoa nut oil is being adulterated with sesamé oil, cotton seed oil, etc. The colour reactions which he proposes for their detection are not required, as the usual tests, such as saponification value, iodine value, etc., readily reveal any adulteration that may have been practised. Owing to the great similarity of cocoa nut oil to palm kernel oil, and the other oils of the cocoa nut oil group, the detection of palm kernel oil in cocoa nut oil, and *vice versa*, is a very difficult problem requiring extended research. Since cocoa nut oil and palm kernel oil have nearly the same price, and since the uses they are put to are practically identical, the examination of cocoa nut oil for admixtures with palm kernel oil, and *vice versa*, is but rarely required. This problem may assume importance in the examination of edible fats with a view to ascertaining their origin, as the properties of palm kernel oil and cocoa nut oil differ somewhat. It should be pointed out that attempts are made to impart to edible cocoa nut oil a more desirable consistence by adding paraffin wax, or heavy paraffin oil. This addition is easily detected by determining the amount of unsaponifiable matter (cp. also "Margarine," Vol. III. Chap. XV.). *Arnold*[1] found recently in an edible cocoa nut oil (or palm kernel oil) 3·9 per cent of unsaponifiable matter, which consisted of a viscous yellow liquid showing in the butyro-refractometer, at 40° C., 74·4 "degrees," having the saponification value nil, and the iodine value 2·65.

(*h*) The fat from *Cocos acrocomoides*, Dr., from Brazil was examined by *Niederstadt*.[2] Its iodine value was 4·8 and the saponification value 292·8. The exceedingly high saponification value was probably due to the rancid state of the specimen, as its acid value was 131.

The *Reichert-Meissl* value of the sample was not determined; most likely it would have approximated that of the other fats belonging to the cocoa nut oil group.

(*i*) TONKA BUTTER

This fat, stated to be derived from the tonka bean *Coumarouna excelsa*, would also appear to belong to the cocoa nut oil group, on account of its high saponification value in association with a high *Reichert-Meissl* value.

The following characteristics were ascertained by *Duyk*[3]:—

Specific gravity at 100° C.	0·888
Melting point	28° C.
Saponification value	257
Reichert-Meissl value	5·4
Butyro-refractometer, "degrees"	47
Critical temperature of dissolution	32·5° C.

[1] *Zeit. f. Unters. d. Nahrungs- u. Genussm.* 1908, xv. 280.
[2] *Berichte d. deutsch. Pharm. Ges.* 1902, 144. [3] *Répert. Pharm.* 1908, 193.

This fat is becoming an article of commercial importance in the Indies, and is said to be used there for flavouring dietetic articles.

JAPAN WAX, JAPAN TALLOW

French—*Cire du Japon ; suif végétal vert.* German—*Japanwachs, Sumachwachs, Japantalg.* Italian—*Cera giapponesa.*

For tables of characteristics see pp. 528, 529.

Japan wax is obtained from the berries of several species of the sumach tree, viz. — *Rhus*[1] *succedanea*, L., *R. acuminata*, D. C., *R. vernicifera*, D. C., *R. sylvestris*, Sieb. et Zucc. The first three species grow chiefly in China, the last named one flourishes especially in the western provinces of Japan. *R. succedanea* occurs also in Indo-China (Tonkin, North Annam, Cambodja) and in India (Sikkim, Nepal, Butan, and Kashmir). In China, Japan, and Tonkin the trees are grown chiefly for the sake of the lacquer they exude. The Japan wax is a by-product of the lacquer industry, and is only prepared in India and China.

The following data, due to *Rein*,[2] show the difference between the berries of *Rhus succedanea* and *Rhus vernicifera* :—

	Rhus succedanea.	*Rhus vernicifera.*
100 berries weigh . . .	8·75 gr.	12·80 gr.
The epidermis forms . .	5·7 per cent.	4·7 per cent.
The mesocarp „ . .	39·3 „	42·4 „
The endocarp „ . .	55·0 „	52·9 „
Japan tallow (by extraction with ether) . . .	24·2 per cent.	27·0 per cent.

The seed consists of a small kernel surrounded by a greenish, striated, shrivelled mass. In China the fatty matter is prepared in the same manner as *mou-iéou* (see "Vegetable Tallow of China," p. 484). From 48 kilos. of seed 5-7 kilos. of the wax (known in China under the name *Tsi-la*, *i.e.* wax of Tsi) are obtained.

The manufacture of Japan wax is carried out in a somewhat crude fashion, by storing the berries in straw until they have fully matured, then crushing them by hand in a wooden funnel-shaped trough, and winnowing them to separate the husks. The powdered mass so obtained is put into hempen sacks, and then subjected to pressure in wooden wedge presses.

With the growing demand for Japan wax the aim has been to increase the output ; this is accomplished by mixing the press residue, or even the ground berries, with a certain proportion (usually 10 per

[1] The oil from *Rhus glabra* has been described above, table facing p. 332.

[2] *Industries of Japan*, 1889, p. 161.

cent) of perilla oil (see p. 39). This practice has been on the increase during the last ten years; therefore the discrepancies in the iodine values recorded in the table of characteristics are readily explained. The samples analysed by *Hübl* and by *Lewkowitsch* date back some decades. Those commercial samples which have higher iodine values undoubtedly contained some perilla oil. Since perilla oil has a very high iodine value, it is evident that a small quantity only is required to raise the iodine value of a commercial specimen.

The berries yield from 15 to 25 per cent of a coarse, greenish, tallow-like mass. This is refined by remelting, pressing through cotton sacks, and allowing the fat to drop into cold water. The thin flakes of wax are then bleached by exposure to the sun in shallow baskets (in a similar manner as is done in the process of bleaching beeswax), the material being frequently turned over and sprinkled with water. Finally the wax is melted and cast into slabs. In this form (termed in Japan *Ki-yu*) it is exported to Europe.[1]

The chief market for Japan wax is Kobe. In this town and in Osaka the three most important refineries are situated. It is stated that an average harvest yields about 2400 tons of crude wax. Older statistics, of the years 1900, 1901, 1902, give the quantities of Japan wax exported as 222, 240, 252 tons respectively. According to the latest statistical data of the Japanese Government the following quantities were exported in the years 1905 and 1906:—

Year.	Total.		Exports to				
	Quantity. Kin.	Value. Yen.	Hongkong. Kin.	England. Kin.	Germany. Kin.	America. Kin.	Manila. Kin.
1905 . .	3,158,188	804,299	838,430	365,301	471,970	691,555	56,343
1906 . .	3,913,626	1,092,447	917,651	496,692	797,141	812,218	118,667

(1 kin = 600 grms.; 1 yen = 2s. 0½d.)

It is hardly to be expected that the production of Japan wax can be largely extended, for it takes seven to eight years for the wax-tree to grow to maturity; and if the tree promises to be a fruitful source of lacquer, this leads to its sacrifice as a source of wax.

The exported Japan wax is a pale yellow hard substance, of conchoidal, somewhat lustrous fracture. It has a wax-like consistence, and can be easily kneaded between the fingers. Its odour recalls that of tallow and beeswax.

On keeping, Japan wax turns deep yellow and becomes coated with a white powder consisting of microscopical prismatic needles. Under the microscope Japan wax exhibits a crystalline structure.

[1] In Europe it is sometimes termed "*Tertia*" (cp. "Prima" and "Secunda," "Vegetable Tallow of China").

Physical and Chemical Characteristics of Japan Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·975	Dieterich	50·8	Rüdorff	50·4-51	Rüdorff	220	Hübl	4·2	Hübl
15·5	0·984-0·993	Allen	53	Allen	56	Allen	214-221·3	Allen	4·9-6·6	Lewkowitsch
			48·5	Eberhardt			221·6	Henriques	8·3-8·5	Geitel and van der Want
22	0·9692	Eberhardt			(cp. p. 530)		217·5-237·5	Geitel and van der Want		
,,	1·002	,,								
60 (water 15·5 = 1)	0·9018	Allen			52-53	Eberhardt			10·6-11·3	Bernheimer and Schiff
					52·6-53·4	Bernheimer and Schiff	220·3-222·1	Bernheimer and Schiff	13·1-15·1	Ahrens and Hett
98-99 (water 15·5 = 1)	0·8755	,,								
Bleached Japan Wax.										
22	0·9749	Eberhardt								

Refractive Index in Butyro-refractometer, observed at 84° C. and calculated to 40° C. :—47·6-49·7 "degrees" (Berg, *Chem. Zeit.* 1903, 755).

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Mean Mol. Weight.	
Per cent.	Observer.	At 98°-99° C. (Water 15·5 = 1.)	Observer.	°C.	Observer.	°C.	Observer.		Observer.
89·8	Lewkowitsch	0·848	Allen	53·0-56·5	Allen	56-57	Allen	265·3	Allen
90·62-90·66	Geitel and van der Want			Titer Test.		59-62	Eberhardt	257·6	Harris[2]
								262-263	Geitel and van der Want
						54-56	Parry[1]		
				58·8-59·4	Lewkowitsch				

The numbers for the specific gravity recorded in the table vary considerably; this is no doubt due to the samples having been derived from different sources.

Kleinstück[3] determined the specific gravity of several samples of Japan wax at different temperatures, and states that its density is equal to that of water at 16°-18° C.; below 16° C. it is heavier, and above 18° C. lighter than water. Japan wax which has been freshly melted has a higher specific gravity than the normal one, the density only becoming normal after keeping for some time. This phenomenon is due to the coëfficient of expansion of Japan wax being higher than that of water, as is shown in the following table due to *Kleinstück*:—

Specific Gravity of Japan Wax compared with that of Water

Temperature. °C.	Japan Wax.		Water.
	Kept for some time.	Freshly melted.	
4	...	...	1·00000
6·5	...	1·00237	0·99995
7·2	1·00737	...	0·99991
17·0	...	0·99123	0·99884
17·5	0·99846	...	0·99875
23·0	...	0·98747	0·99762
26·5	0·98615	0·98683	0·99674

[1] Samples, *Chemist and Druggist*, 1905, 34.

[2] Determined in the author's laboratory; the fatty acids had been previously freed from unsaponifiable matter. This specimen of Japan wax contained 1·1 per cent of unsaponifiable.

[3] *Journ. Soc. Chem. Ind.* 1890, 1072.

The melting points recorded in the table vary considerably. *Rouber's*[1] statement that Japan wax has two melting points, inasmuch as a specimen of the normal melting point melted at 42° C. immediately after solidification is due to the phenomenon described in Chap. I. *Eberhardt* also found that a specimen of the melting point 53° C. melted at 48°-49° C. after rapid cooling.

Japan wax is insoluble in cold alcohol, but dissolves readily in boiling alcohol, separating on cooling almost completely as a granular, crystalline mass. Like all other fats it dissolves easily in ether, benzene, and petroleum ether. The following amounts of unsaponifiable matter were found :—

Unsaponifiable. Per cent.	Observer.
1·14	Allen and Thomson
1·1	Harris[2]
1·48-1·63	Geitel and v. der Want

In a 10 per cent chloroform solution Japan wax proved to be optically inactive.[3]

Japan wax consists chiefly of palmitin and free palmitic acid. Besides these constituents, it also contains small quantities of dibasic acids (see Vol. I. Chap. III.) and of soluble acids.[4] *Geitel* and *v. der Want* found 4·66 to 5·96 per cent of soluble acids. Stearic and arachidic acids, previously stated to occur in Japan wax, could not be detected by *Geitel* and *v. der Want.* On distilling the insoluble Japan wax fatty acids, first under a pressure of 15 mm. up to 250° C., to remove the bulk of palmitic acid, then purifying the residue by crystallising it from 75 per cent alcohol and fractionating the recrystallised product in the vacuum of the cathode light, the remainder of the palmitic acid distils over at 135°-180° C. The higher fractions obtained subsequently were found to consist chiefly of japanic acid, which was accompanied by smaller quantities of its lower homologues, $C_{19}H_{36}O_4$ and $C_{20}H_{36}O_4$. These acids were identified by the composition of the hydrocarbons obtained from them (see Vol. I. Chap. III.). 1000 grams of Japan wax yielded about 6 to 7 grams of mixed dibasic acids.[5] The dibasic acids very likely occur as mixed glycerides (*Geitel*); as an example may be given the formula of the mixed glyceride that would be formed by the combination of japanic and palmitic acids with glycerol :—

$$C_{20}H_{40}\begin{matrix}\diagup CO\,.\,O\\ \diagdown CO\,.\,O\end{matrix}\diagdown\!\!\diagup C_3H_5.$$
$$\qquad\qquad C_{16}H_{31}O\,.\,O\diagup$$

[1] *Journ. de Pharm.* [4] 16 (1872) 20.

[2] Determined in the author's laboratory.

[3] *Chem. Zeit.* 1906, 711.

[4] Engelhardt expressed the opinion that the soluble acids consist in the main of isobutyric acid ; this stands, however, in need of confirmation.

[5] Schaal, *Berichte*, 1907, 4786.

The amounts of free fatty acids in commercial samples vary considerably, as is shown in the following table :—

Free Fatty Acids. Per cent.	Observer.
9·13	Hübl
3·87	Nördlinger
8·96	Allen
9·03	,,
12·72	,,
9·40	Harris[1]
10·9-16·4	Geitel and v. der Want

Commercial Japan wax contains from 0·02-0·08 per cent of ash.

Japan wax is readily distinguished from true waxes by its saponification value, and by its yielding glycerol on saponification; hence the name Japan tallow would appear to be preferable. Its detection in beeswax will be described under "Beeswax."

Adulteration of Japan wax with other fats is easily detected. The presence of tallow will be indicated by a low melting point and a high iodine absorption of the sample.

Commercial Japan wax is frequently adulterated with from 15 to 30 per cent of water.[2] *La Wall*[3] found in a number of commercial samples starch to the extent of 20 to 25 per cent. On treating the adulterated wax with a solvent (Vol. I.) the fat only is dissolved. A rapid method to detect starch qualitatively is to moisten a freshly cut surface with iodine solution.

Japan wax is largely used for waxing floors, and as a constituent of polishes. Like beeswax and other animal waxes it forms an emulsion with water, and is therefore used for currying leather.[4] The difficulties which Japan wax fatty acids offer to their application as candle material have not yet been overcome.

MYRTLE WAX, LAUREL WAX, BAYBERRY TALLOW

French—*Cire de Myrica.* German—*Myrtenwachs, Myricawachs.*
Italian—*Cera mirica.*

For tables of characteristics see p. 533.

Myrtle wax is obtained from the berries of various species of *Myrica.* In North America, where the Myrica shrubs are common along the Atlantic sea-coast, the myrtle wax is obtained from *Myrica cerifera*, L., and *Myrica carolinensis*, Willd. In South America, notably in New Granada and Venezuela, it is obtained from *Myrica arguta,*

[1] Determined in the author's laboratory.
[2] Wimmel, *Zeit. d. öst. Apothekervereins*, 1867, v. 350.
[3] *Journ. Soc. Chem. Ind.* 1897, 247. [4] *Ibid.* 1898, 14.

Kunth, and *Myrica caracassana*, Humb., Bonpl. et K., and in South Africa (Cape Colony[1]) from *M. quercifolia*, L., *M. cordifolia*, L., *M. laciniata*, Willd., and *M. serrata*, Lam. In Abyssinia myrtle wax is obtained from *M. ethiopica*, L.

The myrica fruits are of the size of a pea, and are covered with a snow-white crust of fat, which is permeated with brown or black spots.

The method of preparing the wax is a very primitive one, and consists in boiling the berries in water, when the melted fat rises to the top. This is skimmed off, poured into shallow vessels, and crudely purified by remelting over water. One shrub furnishes 10-15 kilos. of berries, yielding on a practical scale about 20 per cent of myrtle wax. The commercial myrtle wax has a green colour (due to chlorophyll?); on exposure to the air the uppermost layers are bleached to a whitish mass.

Smith and *Wade*[2] confirmed *Chittenden* and *Smith's*[3] earlier statement that the myrtle wax fatty acids consist chiefly of palmitic acid. By recrystallising myrtle wax four times from petroleum ether, *Smith* and *Wade* obtained pure palmitin of the melting point 62·5° C., saponification value 209·4, and refractive index 1·4380 at 80° C. They further showed that by following *Hehner* and *Mitchell's* method no stearic acid was obtained. Judging from the low iodine value, only small proportions of olein can be present.

Smith and *Wade* observed notable changes in the melting point; in the course of four months there occurred a rise of 4·45° C. in the melting point. This phenomenon may be explained by the freshly melted palmitin having been converted, on standing, into its crystalline form (cp. Chap. I.).

The acid values of two specimens of myrtle wax examined by *Deering* were 3 and 4·4. The acid value of the specimen examined in the author's laboratory was 3·6. The amount of unsaponifiable matter found by Cocking[4] was 2·51 per cent.

Myrtle wax worked up by itself does not yield useful candles; it can, however, be employed in a proportion of 20-25 per cent as an addition to other candle material. In the United States "bees-wax" candles are made which contain a notable amount of myrtle wax. Myrtle wax should prove useful in the manufacture of soap. In this connection it may be mentioned that *Chevreul* first prepared myrtle wax soap on a laboratory scale.

[1] In the *Bulletin Imperial Institute* (1906, 301) the statement was made that no proper organisation exists as yet for collecting the myrtle berries in Cape Colony. Since then, the Cape Government has leased the Crown lands on which the berries used to be collected. The result has not, however, so far been satisfactory, and the quantities exported have decreased.

[2] *Journ. Amer. Chem. Soc.* (1903) 629.

[3] *Amer. Chem. Journ.* 6 (1884), 217; *Bulletin Imperial Institute*, 1906, 365.

[4] *Chemist and Druggist*, 1908, 74.

Physical and Chemical Characteristics of Myrtle Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 80° C.	Observer.
15	0·995	Allen	39-43	Allen	40-44	Allen	205·7-211·7	Allen	1·95	Lewkowitsch	0·5	Smith and Wade	1·4363	Smith and Wade
22 (water at 15·5=1)	0·9806	Smith and Wade	45	Smith and Wade	48	Smith and Wade	217	Smith and Wade	3·9	Smith and Wade				
98-99 (water at 15·5=1)	0·875	Allen					212·3	Cocking						
99 (water at 15·5=1)	0·878	Smith and Wade												

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Mean Molecular Weight.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.		Observer.
...	...	46	Allen	47·5	Allen	243	Allen
89·7[1]	Cocking	...	...	48·5	Cocking	241·4	Cocking

[1] It is doubtful whether 89·7 includes the amount of unsaponifiable.

Dika Fat Group (see Appendix)

(*a*) DIKA FAT, DIKA BUTTER, DIKA OIL, OBA OIL, WILD MANGO OIL

French—*Beurre de dika (etc.)*. German—*Dikafett*.
Italian—*Sego di dika*.

Dika fat is obtained from the seed-kernels of various kinds of *Irvingia* (*I. gabonensis*, Aubry-Lecomte; *I. Barteri*, Hook. fil.). Also *Mangifera gabonensis* is recorded in the literature as a tree yielding dika fat, but it appears that *Mangifera gabonensis* is identical with *Irvingia gabonensis*. These trees, belonging to the *Irvingia* family, are indigenous to the West Coast of Africa, from Sierra Leone to Gaboon. They are termed by the natives "udika," "dika," "dita," and "oba." The fruits are known in Gaboon as "iba."

The natives remove the shell by cracking the nuts, grind the kernels in their fresh state with a little water, pepper, and salt, and work them up into cakes. These cakes form a staple article of food amongst the natives; they are known under the name "dika bread,"[1] "dika chocolate," or "gaboon chocolate."

Another way of preserving the kernels is to crack the nuts and dry the kernels, which split readily into halves, in the sun. These sun-dried kernels can be kept for a long time without undergoing deterioration.

By boiling the kernels with water and skimming off the oily layer the natives obtain their dika butter.

The author[2] examined a considerable quantity of both nuts and sun-dried kernels. The seeds were stated to be those of *Irvingia Barteri*, Hooker, and were sent from South Nigeria to the Imperial Institute. The nuts were in so advanced a state of mouldiness that it was useless to extract the fat from them. Sound nuts are stated to yield 20 per cent of kernels.

The sun-dried kernels contained 54·3 per cent of fat. This fat was in a comparatively fresh state, as the percentage of free fatty acids amounted to 3·35 per cent only.

The following numbers were found:—

Fat

Specific gravity at 40° C. (water at 40° C. = 1)	0·9140
Melting point (capillary tube)	38·9° C.
Solidifying point	29·4-27·2° C.
Saponification value	244·5
Iodine value	5·2
Reichert-Wollny value	0·42 per cent.
Unsaponifiable matter	0·73 ,,

[1] An examination and illustration of "dika bread" is published by Dr. E. Heckel, 2e *Mémoire des Annales du musée et de l'institut colonial de Marseille*; cp. also *Bulletin Imperial Institute*, 1904, vol. iv. No. 1. A "dika bread" is also prepared from the roasted seeds by mixing them with those of *Fegimaura africana*, Pierre, and of *Pentaclethra macrophylla*, Benth. (see "Owala Oil," p. 242). Drabble, *Quart. Journ. Inst. Comm. Research in the Tropics*, 1908, 20.

[2] *Analyst*, 1905, 394.

Fatty Acids

Mean molecular weight	214
Solidifying point	34·8° C.
Stearic acid	absent

The iodine value is much lower than the one given by *Dieterich* —viz. 30·9 to 31·3. Since *Dieterich* also records a low melting point—viz. 29°—he evidently did not have genuine dika fat in his hands. The iodine number found by the author is in good agreement with *Oudemans'*[1] statement that dika fat consists of laurin and myristin only, to the exclusion of olein. It should, however, be mentioned that the absence of olein was only inferred by him from the fact that no ether-soluble calcium salt could be obtained. *Heckel* confirmed *Oudemans* in that he could not obtain an ether-soluble lead salt; but, of course, this cannot be taken as proof for the absence of oleic acid.

The absence of stearic acid, the low mean molecular weight of the total fatty acids, and the somewhat large quantity of insoluble volatile acids obtained in the *Reichert-Wollny* test, confirm in the main the composition given by *Oudemans*. A small proportion of olein must, however, be allowed. Since *Oudemans* showed by careful examination that palmitic acid is absent, the fat may be taken as consisting of myristin, laurin, and a few per cent of olein.

Dika fat has not yet been prepared on a manufacturing scale, the difficulty of importing the sun-dried kernels being still greater than that of importing palm kernels. The fat would be useful for the soap and candle industries, and might also prove suitable for edible purposes. Indeed, *Sachs*[2] states that it is used as a "chocolate fat."

(*b*) TANGKALLAK FAT, TANGKALLAH FAT

French—*Suif de Tangkallak.* German—*Tangkallakfett.*
Italian—*Burro di tangkallak.*

For table of characteristics see p. 537.

This fat is obtained from the fruits of *Lepidadenia Wightiana*, Nees, Bl. (*Cylicodaphne sebifera*, *Cylicodaphne Litsœa*, Bl., *Tetranthera callophylla*, Miquel, *T. laurifolia*, Jacq., *Litsœa sebifera*, Pers., *Sebifera glutinosa*, Lour.), a tree indigenous to Western Java, and at present common in Indo-China. It is also found in Réunion under the name *bois d'oiseau.*

The statements occurring in the literature regarding the chemistry of tangkallak fat are conflicting, and it would therefore

[1] *Journ. f. praktische Chem.* 81, 356. [2] *Chem. Revue*, 1908, 9.

appear that the several observers who have published notes on this fat, examined specimens from different species of plants. *Van Gorkom*[1] stated that the fat consists of 15 per cent of olein and 85 per cent of laurin. This was confirmed by *Oudemans*.[2] Latterly *Greshoff*[3] found in the fleshy part of the fruit of a *Cylicodaphne* 36·5 per cent of a fat melting at 37° C., and in the seeds 52 per cent of a fat of the melting point 44° C. *Sack*,[4] by extracting the seeds with ether, found 47·3 per cent of a fat which yielded by repeated crystallisation from alcohol a glyceride melting at 45° C. This was judged by *Sack* to be pure trilaurin. From the data given by him the author calculates the iodine value of the fat to be 11·54, which agrees fairly with his statement that tangkallak fat contains 13·4 per cent of triolein. The remaining 86·6 per cent is considered by *Sack* to be trilaurin.

Recently *Schroeder*[5] examined the fat from genuine seeds of the tangkallak tree obtained from Buitenzorg (Java). The seeds yielded 51 per cent of fat on extraction with petroleum ether. The numbers obtained by *Schroeder* are collated in the table of characteristics with those of *Sack* (see p. 537). The iodine values speak against the identity of the two specimens examined by *Sack* and by *Schroeder*. The amount of insoluble fatty acids + unsaponifiable was found by *Schroeder*, as the mean of three determinations, to be 76·1 per cent, which points to the fact that large quantities of lauric acid had been washed away. The amount of unsaponifiable matter was 1·44 per cent. The *Reichert-Meissl* value of 1·47 would appear to be due to small quantities of volatile fatty acids, lower than lauric acid, inasmuch as the saponification value of the fat ascertained by *Schroeder*—268·2—is higher than the saponification value of laurin. The fat would, therefore, appear to consist of practically pure laurin. Besides lauric acid, *Schroeder* found small quantities of a liquid fatty acid which had the iodine value 68·65; most likely this was oleic acid, holding in solution some lauric acid. According to *Schroeder*, tangkallak fat consists of 96·4 per cent of laurin and 2·6 per cent of olein.

The specimen examined by *Schroeder* had the acid value 3·35. The fat dissolved in 15 parts of absolute alcohol at 20° C.

Tangkallak fat is used in Java for the manufacture of candles. One tree is stated to provide annually sufficient material for the production of 500 candles.

[1] *Nat. Tijdschr. Ned. Ind.* xviii. (1858), 410.
[2] *Zeits. f. Chem.* 1867, 256. [3] *Teysmannia*, i. (1890), 127.
[4] *De indische Mercuur*, 28th April 1903; *Pharm. Weekblad*. 1903, 4.
[5] *Archiv der Pharm.* 243 (1905), 631.

[TABLE

Physical and Chemical Characteristics of Tangkallak Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.	
At 41° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
...	...	...	...	37	Sack	...	...
0·8734	Schroeder	27	Schroeder	46·2	Schroeder	268·2	Schroeder

Physical and Chemical Characteristics of Tangkallak Fat—continued

Iodine Value.		Reichert-Wollny Value.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
11·54	Sack [1]	...	...
2·28	Schroeder [2]	1·47	Schroeder

[1] Calculated by the author from the proportion of triolein given by Sack.

[2] By means of iodine bromide.

(*c*) CÁY CÁY FAT, COCHIN-CHINA WAX, IRVINGIA BUTTER

French—*Beurre d'Irvingia ; beurre de Cäy Cäy ; beurre de l'arbre à chandelle.* German—*Kotschinchinawachs.* Italian—*Sego di Cäy Cäy.*

Cáy Cáy fat (*i.e.* candle tree fat) is obtained from *Irvingia Oliveri*, Pierre, *Irvingia malayana*, Oliv., or *Irvingia Harmandiana* ; *Buchanania fastigiata*, H. Baillon. The Cáy Cáy is a tropical tree indigenous to Cochin China and Cambodja ; its habitat is in the forest. *Irvingia malayana* is chiefly found in Cambodja, whereas *Irvingia Oliveri* is characteristic of Indo China (Cochin China). Both trees are known to the natives under the name "candle tree" or "Indo-Chinese wax" tree. The tree is unknown in Tonkin and in the northern part of Annam, whereas it still grows in the southern province of Annam (Binhthuanh). It produces a very large number of fruits which mostly rot away unused for want of facilities of transport. The fruits fall off the tree in July and August, and are allowed by the natives to lie for about two months, whereby the fibrous mesocarp becomes softened. They are then placed in the sun to dry, and the shells are removed by a knife or a hammer. The difficulty of removing the shell seems to have militated hitherto against proper commercial exploitation. The kernels are exposed to the sun to dry, when a brown skin surrounding them can be easily removed. The shelled kernels are then pounded in a mortar and the pounded mass placed on a layer of bamboo over pots of boiling water, so that the steam warms it. It is then packed in bags and expressed in a crude native press. The still liquid fat is then poured into very primitive candle machines, consisting of bamboo tubes fitted with cotton wicks. A still less pure kind of Cáy Cáy fat is obtained by boiling the pounded kernels with water, and skimming off the fat as it separates.

It is stated that the nuts yield 20 per cent of kernels, and that one kilo. of the kernels gives four candles, two large ones and two small ones, which weigh about 430 grams, so that the yield of fat from the kernels would be about 43 per cent. *Vignoli*[1] obtained in the laboratory from the kernels 52-56 per cent of fat (by extraction with carbon bisulphide). Considering the extremely crude method practised by the natives, the yield they obtain is a very good one. The residual cake is mostly used as fuel or as cattle food, or for manuring the land.

Cáy Cáy fat has a greenish-yellow colour, undoubtedly due to impurities caused by the crude process of production. On exposure to the air the fat is bleached and becomes white. *Vignoli* stated that the fat consists of 70 per cent of saturated acids and 30 per cent of oleic acid. *Heckel*, who again examined the Cáy Cáy fat, gives its melting

[1] *École supérieure de pharmacie de l'académie de Montpellier*, Thèse, 1886.

point as 39·5° C. The mixed fatty acids melted at 37·2° C. By repeated crystallisation of the mixed fatty acids from acetone, an acid was obtained which melted at 53·6° C. *Heckel* takes this as proof that the fatty acid is myristic acid. He further states that oleic acid is absent, and that the total fatty acids consist of a mixture of 30 per cent of myristic and 70 per cent of lauric acid.

As all these statements stood in need of confirmation, *Bontoux*[1] examined genuine seeds of *Irvingia Oliveri*, and two Cáy Cáy fats prepared by the natives in Cambodja. All the specimens were authenticated, being supplied from the exhibits of the Colonial Exhibition of Marseilles, 1906. The seeds were in perfect condition; 100 seeds weighed 360 grams, and yielded 78·14 per cent of shells and 21·86 per cent of kernels. The latter were dry, had a pleasant taste, were free from rancidity, and yielded, on extraction with petroleum ether, 60·45 per cent of an almost white fat of pleasant taste (after purification). The Cambodja fats, although over two years old, were only slightly rancid.

The extracted fat, as also the native fats, had the consistence of beeswax; in contradistinction to this substance they had a crystalline structure, and hence were more friable than beeswax. The following numbers were determined in these fats by *Bontoux*:—

	Fat extracted in the Laboratory.	Native Preparations.	
		No. 1.	No. 2.
Fat—			
Melting point	39·7° C.	38·2° C.	38·4° C.
Solidifying point	31° C.	31·2° C.	31·8° C.
Saponification value	235·0-235·6	236·3	237·4
Iodine value	6·7-6·8	4·1-4·2	4·9-5·1
Acid value	0·89	23·5	34·9
Fatty Acids—			
Fatty acids + unsaponifiable	94·0%	93·4%	93·2%
Solidifying point (titer test)	36·6° C.	...	36·4° C.
Neutralisation value	253·0	...	250·2
Mean molecular weight	222	...	224

The best qualities of Cáy Cáy served formerly as an edible fat in place of butter, and cakes of such butter used to be largely sold in the markets of Saïgon and Cambodja. At present hardly any edible fat is prepared, most of the product being made into candles for local use, as described above. The crude fat for this purpose is sold under the name of Cáy Cáy wax. The importation of paraffin oil into Indo-China has, however, considerably reduced the demand for candles, and the output of Cáy Cáy fat has consequently greatly decreased.

[1] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires*, traduit par E. Bontoux, vol. ii. p. 1138. (See Appendix.)

(*d*) KUSU OIL [1]

French—*Huile de Kusu.* German—*Kusuöl.*
Italian—*Olio di Kusu.*

Kusu oil is contained in the fruit of the camphor-yielding tree *Cinnamomum Camphora*, Nees (*Lauraceæ*). The seeds are about 0·5 cm. in diameter, and weigh on an average 0·1 gram. They contain 6·78 per cent of moisture, 42·4 per cent of fat, and 2·1 per cent of ash. The fat which was prepared in the laboratory by powdering and pressing the seeds at a somewhat elevated temperature forms a white crystalline mass, having a slight aromatic odour which recalls that of cocoa nut oil. The following characteristics were ascertained :—

Specific gravity at 25° C.	0·9267
Specific gravity at 100° C.	0·8760
Melting point	22·8° C.
Saponification value	283·8
Iodine value	4·5
Reichert-Meissl value	0·53
Refractive index at 25° C.	1·4517

The acid value of the sample was 4·70.

The amount of insoluble acids + unsaponifiable found was 81·8 per cent; although 2 litres of water were used for 3 to 4 grams, the wash water still contained soluble acids. The mixed acids used in the determination of the following numbers were obtained by washing with a 10 per cent solution of common salt—

Fatty Acids

Specific gravity at 100° C.	0·8412
Melting point	21° C.
Neutralisation value	292·8
Mean molecular weight	191·6
Iodine value	5·1

From the foregoing numbers it may be concluded that the chief constituent of the oil is laurin. The fat would thus resemble cocoa nut oil and its congeners, but differs notably from them by its low *Reichert* value. The fat seems to be more nearly related to dika fat, tangkallak fat, and Irvingia butter, all of which are characterised by high proportions of laurin.

[1] Tsujimoto, *Journ. Coll. Engin.* Tokyo, Imp. Univ. Japan, 1908, 86.

Lesser Known Vegetable Fats, see table opposite.

luble +Un- ifiable.	Reichert-Meissl Value.	Refractive Index.	Melting Point of Fatty Acids.	Acid Value.	Observer.
..	...	...	...	...	Niederstadt
..	...	...	...	...	,,
..	...	...	...	...	,,
..	...	...	...	72·2	,,
..	...	...	...	13·1	,,
..	...	...	...	16·55	,,
·8	0·33	1·4584	...	15·40	Crossley and Le Sueur
..	...	...	...	7·8	Niederstadt
..	...	..	...	51·5	,,
..	...	...	...	83·7	,,
..	...	...	48-49 [4]		
..	...	...	...	...	Pairault [8]

ames "*Lumbo*," "*Pyal*," "*Charolee.*" The seeds, known as "chirongi," are eaten as

173.
bourhood of Libreville. Cp. Heckel, *Les Matières grasses*, 1908, 1002.
ng at 58°-59° C., 44° C., and 38° C. respectively.
[6] The plant has also been introduced into America.
extended to most tropical countries ; it is common in Indo-China.
st. 1908 (25), 778.

Face page 540, *Vol. II.*

2. Animal Fats

The fats described under this head vary in their hardness, like the vegetable fats, in inverse proportion to the amount of unsaturated fatty acids they contain, or, in other words, to the amount of iodine they absorb. Butter fat, in a similar fashion as the fats of the cocoa nut oil group, occupies an exceptional position owing to its high proportion of glycerides of volatile acids. In a system based on similarity of chemical composition butter fat would be classed with the cocoa nut oils, but it is more convenient to retain the subdivision into vegetable and animal fats, inasmuch as these two classes can be readily differentiated by the phytosteryl acetate test.

The unsaturated fatty acids of the animal fats were until recently considered to consist of oleic acid only, and this was thought to constitute an important natural difference between vegetable and animal fats. It has, however, been shown that some animal fats contain less saturated fatty acids than oleic acid. Indeed, the presence of linolic acid has been proved in the case of lard (*Fahrion*) and hare fat (*Kurbatoff*), by identifying amongst the oxidation products of the liquid fatty acids sativic acid, and, in the case of lard, by the isolation of linolic tetrabromide (*Farnsteiner*). Furthermore, *Farnsteiner* has shown that even small quantities of linolenic acid occur in lard and tallow (for a probable explanation, see below). From icebear fat 9·3 per cent of fatty acids were isolated, the iodine value of which reached as high a figure as 244·4.

We are, therefore, in a position to discriminate drying, semi-drying, and non-drying fats, similarly as in the case of vegetable oils and fats, and also to establish among the animal oils and fats all gradations from fish and liver oils down to the hardest fats, containing very small proportions of glycerides of unsaturated fatty acids. Whilst the marine animal oils simulate the drying oils, we have a certain class of animal fats, represented by icebear fat, blackcock fat, hare fat, wild duck fat, which may be likened to semi-drying oils. Reasoning by analogy, we must ascribe these drying properties to the occurrence of fatty acids, which are less saturated than oleic acid.

The presence of highly unsaturated fatty acids in icebear fat suggests the inference that the nature of the food has great influence on the chemical composition of the body-fat. On this assumption *Voit's* opinion that each animal is characterised by a specific kind of fat is no longer tenable. Although this question would appear to belong to the domain of physiology, its discussion is germane to our subject, inasmuch as this is a matter of the greatest importance to the analyst who has obtained abnormal numbers in the examination of a lard or butter fat.

It is well known that if large quantities of one particular fat are given with the food, such fat is liable to pass into the body-fat

of the animal.[1] Thus it has been shown that the fat from dogs who were given considerable quantities of linseed oil in their food had acquired the peculiar odour of linseed oil, and exhibited distinct drying properties; again, after feeding dogs with rape oil the presence of erucic acid in the fat could be proved (*Radziejewski*). *Munk* has then shown that in dogs that had been kept on starvation rations, subsequent feeding with mutton tallow produced a deposition in the body of a fat very similar to mutton tallow. It has further been ascertained that hogs fed on dried fish yielded lard of a disagreeable fishy taste; moreover, such lard was less hard than that from normally fed hogs. During the last decade or two the practice of feeding the hogs (in America) on maize has produced much "softer" lards than were previously obtained, a fact which must undoubtedly be ascribed to the influence of maize oil. It has also been observed that tallow from cattle fed on oil cakes is softer, *i.e.* richer in olein, than tallow from cattle fed on grass (South American tallow, New Zealand tallow).

Not only does the kind of food influence the character of the *body-fat*, but, as a general rule, the fat given in the food seems also to pass into the *milk-fat*.[2] Thus *Baumert* and *Falke*[3] have shown that on feeding cows with oil-cake obtained from sesamé seed, almonds, and cocoa nut kernels, there were obtained butter fats which showed so remarkable a decrease in their proportions of volatile fatty acids (*Reichert-Meissl* values) that without further investigation the butter fats would have been declared adulterated, inasmuch as the analytical characteristics were those of a mixture of genuine butter fat with very considerable amounts of foreign fats (cp. also "Human Fat," p. 557). The above-mentioned occurrence of linolenic acid in lard and tallow must, therefore, be ascribed to the influence of the food on the body-fat (cp. also "Lard," p. 570; "Butter Fat," p. 690). In order to further illustrate the influence of the fat given with the food, I collate some isolated observations on the fats from certain wild animals, and contrast them with the fats from the same species in a domesticated state.

[1] *Bömer* (*Zeit. f. Unters. Nahrungs- u. Genussm.* 1907, xiv. 93) puts forward the opinion that it is not the fats themselves (that are given with the food) which pass into the body-fat or milk-fat, but rather the fatty acids. This would, of course, mean that the fats are hydrolysed first, that the fatty acids pass through the tissues, and that the fatty acids find glycerol there (either newly formed or derived from hydrolysed fat), which has also passed through the tissues ready to perform the synthesis of fats. Some slight support for this opinion may be found in the experiments of *Pottevin*, as also of *Twitchell* (Vol. I. Chap. II.). *Bömer* thinks that a strong argument in favour of his views (that the fatty acids and not the glycerides themselves pass into the body-fat) is offered by the fact that phyto-terol given with the food does not pass into the body-fat.

The view that fats are hydrolysed to glycerol and fatty acids in the first stage of the digestive process is put forward on the strength of physiological experiments by Levites, *Hoppe-Seyler's Zeit. f. physiol. Chemie*, 49 (1906), 273; 53 (1907), 350; 1908 (57), 46.

[2] Cp. Zuntz and Usson., *Chem. Centralblatt*, 1900, 382; Einecke, *Mitth. d. landw. Inst.* 1903, 559.

[3] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1898, 665. For similar experiments and results obtained by feeding with rice meal, see *Zeit. f. Unters. Nahrungs- u. Genussm.* 1908, xv. 33.

Fat from	Iodine Value.
Rabbit, wild	101·1
,, tame	64·4
Goose, wild	99·6
,, wild, held in captivity 2 years	67·0
,, domestic	67·6
Duck, wild	84·6
,, domestic	58·5
Hog, wild	76·6
,, domestic	66
Cat, wild	57·8
,, domestic	54·5

In the case of wild goose and wild duck, the feeding on fish satisfactorily explains the high iodine values.

As a corollary to the foregoing observations, it may be added that the fat from a chicken fed on milk approximated to the composition of butter fat (high saponification value), although it did not yield a larger amount of volatile fatty acids than ordinary chicken fat (*Zaitschek*).[1] Experiments made by *Weiser* and *Zaitschek*[2] on geese fed with maize showed, however, that the body-fat was not altered,[3] probably because the food was poor as regards content of fat. As a further rule it may be stated that the amount of liquid (unsaturated) fatty acids decreases as the position of the fat approaches the warmest parts of the body.[4]

In view of the change animal fats undergo in consequence of the change of food, it became of great importance to investigate whether phytosterol, if supplied together with a vegetable fat in the food, passes into the body-fat, and may therefore occur in such body-fat side by side with cholesterol. This possibility, under certain conditions, was not excluded, since the colouring matter contained in cotton seed and cotton seed oil passes into the body-fat of hogs, and into the milk-fat of cattle fed on cotton seed cake.

Since all fodders given to domestic animals contain phytosterol, and yet all animal oils and fats examined hitherto have been proved to be free from phytosterol, it might have been concluded, *a priori*, that phytosterol does not pass into the food. It was, however, desirable to investigate this more fully, as through feeding with cake larger doses of phytosterol are introduced into the system than with ordinary fodder. *C. Virchow*,[5] who first inquired into this matter, has shown that on feeding animals (dogs, hogs, etc.) with cotton seed oil and peas, phytosterol could not be detected in the body-fat. Nor

[1] *Pflüger's Arch.* 98, 1903, 614. [2] *Ibid.* 1902, 128.

[3] *Ibid.* 93, 1902, 128. Cp. also Paraschtschuk, *Chem. Centralbl.* 1903, i. 731; Arnold, *ibid.* 1903, i. 531.

[4] Henriques and Hansen, *Biederm. Centr.* 1901, 182; Lemmermann and Linkh, *Landw. Jahrbücher*, 1903, 635. Exceptions to this rule have been observed by Raikow (*Chem. Zeit.* 1904, 272) in the case of bear fat; and in the case of horse fat by Dunlop (*Analyst*, 1907, 318). The fat taken from the kidney bed, which in most animals gives the lowest iodine value, furnished the highest figure yet recorded for horse fat, viz. 110·65 (H. Dunlop).

[5] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1899, 559.

could *Bömer*[1] detect any phytosterol in a butter from a cow fed on sesamé, cocoa nut, and almond cakes; neither could *Fulmer*[2] and *Polenske*[3] detect it in the lards of hogs fed with cotton cake and cotton seed oil respectively, although in the last case abnormally large quantities of oil were given to the pigs (*Farnsteiner*). All the foregoing researches have been confirmed by an exhaustive enquiry of *König* and *Schluckebier*,[4] who carefully examined the body-fat taken from five different parts of the body of young pigs (head, back, leaf, ham, intestines), as also the fat from the liver, brain, and gall. In no case was phytosterol found, cholesterol being the only alcohol contained in the unsaponifiable matter of all these fats.

It was further of great importance to investigate whether those chromogenetic substances of cotton seed oil and sesamé oil that show the characteristic colour reactions of these two oils pass into the body-fat or milk-fat if cotton seed cake or sesamé cake is given with the food. As this question will be fully discussed under the headings of "Lard" and "Butter Fat," it need only be pointed out here that exhaustive investigations have demonstrated the fact that the chromogenetic substance of cotton seed oil does migrate into lard and milk-fat, although *Thorpe*[5] noticed that individual cows vary in their ability to pass the reacting substance into the milk-fat. As regards sesamé oil, the opinions of numerous observers are conflicting, but the evidence goes to show that under certain conditions (which are not fully known yet) the chromogenetic substance of sesamé oil migrates into the milk-fat of mammals. Quite recently *König* and *Schluckebier*[6] demonstrated that on feeding pigs with sesamé cake the substance which gives the *Baudouin* reaction passes into the body fat. This was proved by examining the fat taken from five different parts of the animal (head, back, leaf, ham, intestines) which had served for the experiment.

Other influences which bear on the composition of animal fat, such as the influence of seasons, climate, mode of living, age, state of health, and idiosyncrasy of the animal, will be considered under "Human Fat," "Lard," "Tallow," and "Butter Fat."

Polenske[7] recently made the interesting observation that the difference between the melting and solidifying points is constant for one and the same animal fat, whereas different animal fats exhibit different ("difference") numbers. Thus for a number of tallows the "differences" found were 12·8° to 14·7° C., for goose fat 14·0° to 16·2° C., and for butter fats 11·8° to 14·3° C., whilst lard is characterised by higher numbers, viz. 19·2° to 20·6° C. *Polenske* bases on this observation a method for the detection of lard, as also of tallow, in goose fat. This method is likely to prove useful for the detection of tallow and lard in butter fat.

[1] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1902, 1023.
[2] *Journ. Amer. Chem. Soc.* 1904 (26), 837.
[3] *Arbeit. a. d. kais. Gesundheitsamt*, 1905, 567; cp. also Farnsteiner, Lendrich, and Buttenberg, *Zeit. f. Unters. Nahrungs- u. Genussm.* 1906, xi. 1.
[4] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1908, xv. 642.
[5] *Analyst*, 1898, 257. [6] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1908, xv. 642.
[7] *Arb. a. d. kais. Gesundheitsamt*, xxvi. 3, 1907.

I subdivide the animal fats into: (1) drying, (2) semi-drying, and (3) non-drying fats:—

(1) Drying Animal Fats

Fats.	Source.	French.	German.	Italian.	Specific Gravity.	Saponification Value.	Iodine Value.	
					At 15° C.	Mgrms. KOH.	Per cent.	Observer.
Icebear .	Ursus maritimus	Ours .	Eisbär . .	Orso bianco	0·9256	187·9	147·0	H. Bull
Rattlesnake	Crotalus durissus	Crotale	Klapperschlange	Crotalo .	0·9217	210·9	105·58	Kebler and Pancoast

(2) Semi-drying Animal Fats

Kind of Fat.	Source.	French.	German.	Italian.	Specific Gravity at 15° C.		Solidifying Point.		Melting Point.	
					Fat.	Fatty Acids.	Fat. °C.	Fatty Acids. °C.	Fat. °C.	Fatty Acids. °C.
Blackcock	Tetrao urogallus	Coq de bruyère	Auerhahn	Gallo di montagna	0·9296	0·9374	...	25-28	...	30-33
Lynx	Lynx europæus	Lynx	Luchs	Lince	0·9248	0·9412	...	35	...	35·3
Wild duck	Anas boschas	Canard sauvage	Wildente	Germano reale	...	...	15-20	30-31	...	36-40
Marmot	Arctomys marmota	Marmotte	Murmeltier	Marmotta	0·9183	...	...	27	...	28·5

Semi-drying Animal Fats—*continued*

Saponification Value.	Neutralisation Value. Mgrms. KOH.	Reichert Value.	Iodine Value. Per cent.		Insoluble Acids + Unsaponifiable. Per cent.	Refractive Index. Butyro-refractometer.				Observer.
						Fat.		Fatty Acids.		
Fat.	Fatty Acids.	c.c. $\frac{1}{10}$ normal KOH.	Fat.	Fatty Acids.		°C.	"Degrees."	°C.	"Degrees."	
201·6	199·3	2·10	121·1	120	...	...	...	...	...	Amthor and Zink[1]
190·2	202·7	0·4 (R.M.)	110·6	111·8	95·8	20	70	35	53·9	Schneider and Blumenfeld[2]
198·5	...	1·30	84·6	...	...	45	55·5	45	48·3	Amthor and Zink
197·1	209·6	0·6 (R.M.)	109·1	105·6	95·8	40	59·4	...	...	Gruebler[3]

[1] *Zeit. f. analyt. Chem.* 1897, 1.

[2] *Chem. Zeit.* 1906, 54. The acetyl value of the fatty acids was 7·67.

[3] *Zeit. öster. Vereins*, 1907, No. 52.

HORSE FAT

French—*Graisse de cheval.* German—*Pferdefett.*
Italian—*Grasso di cavallo.*

For tables of characteristics see p. 549.

Fresh horse fat (from *Equus caballus*) is of yellowish colour, and has a buttery consistence. On standing, it separates into a solid and a liquid portion. In its fresh state it is neutral. As the rendering of horse fat is not so carefully carried out as that of other animal fats, remnants of tissue are frequently contained therein; hence it readily becomes rancid.

In a sample of kidney fat stearic acid could not be detected by the method described Vol. I. Chap. VIII. *Farnsteiner* isolated from a specimen of horse fat linolic tetrabromide in a quantity corresponding to 9·9 per cent of linolic acid in the fat. The fat taken from the kidney bed, which in most animals gives the lowest iodine value, furnished the highest figure yet recorded for horse fat, viz. 110·65 (*H. Dunlop*).[1]

The occurrence of linolic acid satisfactorily explains the weak drying properties this fat shows on exposure to the air.

In consequence of the increasing consumption of horse meat, horse fat has become a commercial article. It is used by the poorer classes on the Continent as an edible fat in place of lard, and is no doubt used as an adulterant of more expensive fats. A technical application of horse fat for the coating of calcium carbide in the production of acetylene has been patented by *J. M'Rae.*[2]

The following characteristics for horse fat from various parts of the body[3] have been published:—

[1] *Analyst*, 1907, 318. [2] English patent 25,046, 1905.
[3] As to the foot oil, cp. p. 400.

[TABLE

Horse Fat from	Consistence.	Colour.	Specific Gravity.		Solidifying Point. °C.	Melting Point. °C.	Solidifying Point of Fatty Acids. °C.	Melting Point of Fatty Acids. °C.	Saponification Value.	Iodine Value of		Reichert Value.	Insoluble Acids + Unsaponifiable.	Acid Value.	Refractive Index. Butyro-refracto-meter at 25° C.	Observer.
			At °C.							Fat.	Fatty Acids.					
Kidneys	Salve-like, soft	Golden-yellow	15	0·9320	22	39[1]	30-30·5	36-37	198·7	81·09	83·88	0·33	95·47	1·73	"Degrees."	Amthor and Zink
,,	..	..	..	..	..	..	..	..	..	110·7[2]	..	..	..	..	66	Dunlop[3]
,,	..	..	..	..	..	..	..	..	..	85·4	..	..	..	..		Hehner and Mitchell
,,	..	..	17·5	0·9212	48-47	53-54	..	..	187·6	82·6	84·0	..	..	..		Frühling
,,	..	..	50	0·8987	..	..	..	..	..	..	..	..	..	..		,,
Neck .	Like fresh hard butter	Deep orange-yellow	15	0·9330	30	34-45[1]	32-33	41-42	199·5	74·84	74·41	0·22	95·42	2·44		Amthor and Zink
,, (mane)	..	..	..	..	..	..	..	..	199·1	86·7[2]	..	..	..	..	61·2	Dunlop
,,	..	..	..	..	..	..	..	..	..	90·7[2]	..	..	..	..	61·2	,,
Leaf .	Butter-like	Golden-Yellow	15	0·9319	20	36-37[1]	31-32·5	39-40·5	197·8	81·6	83·37	0·38	94·78	1·84		Amthor and Zink
Back .	..	..	17·5 50	0·9159 0·8963	45-43	52-53	..	..	182·8	79·9	81·4	..	..	..		Frühling
Heart .	..	..	17·5 50	0·9167 0·8948	34-32	40-41	..	..	184·7	77·4	78·3	..	..	..		,,

[1] Capillary tube method.

[2] As to the horse oil obtained from these fats cp. p. 550.

[3] *Analyst*, 1907, 318.

Physical and Chemical Characteristics of Horse Fat

Specific Gravity.			Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index. Butyro-refractometer.		Maumené Test.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 40° C.	Observer.	°C.	Observer.
15	0·9189	Filsinger	20	Lenz	197·1	Filsinger	86·1	Kalmann	1·64-2·14	Kalmann	"Degrees." 53·7	Mansfeld	46-54·2	Gill and Rowe
,,	0·916-0·922	Gill and Rowe	41·8-43·2[1]	Kalmann	195·1-196·8	Kalmann	84	Filsinger						
98-99	0·861	Allen					71·4-72·4	Lewkowitsch					Specific Temperature Reaction.	
100	0·798-0·799	Gill and Rowe					75·1-86·3	Gill and Rowe					95·8-114	Gill and Rowe

[1] Capillary tube method.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
96-97·8	Kalmann	37·3-37·7 33·6-33·7 (Titer test.)	Kalmann Lewkowitsch	37·5-39·5	Kalmann	202·6-202·7	Kalmann	83·9-87·1	Kalmann

Horse Oil.—The liquid portion of horse fat is frequently prepared separately by simple filtration at low temperature. It is sold in commerce as *horse oil* or "animal oil." It must not be identified with horses' foot oil (see p. 400). The following table contains some characteristics of horse oil (*Dunlop* [1]):—

Horse fat from	Colour and Consistence.	Specific Gravity at 15·5° C.	Saponification Value. Per cent.	Iodine Value (Wijs).	Reichert-Wollny Number.	Butyro-Refractometer at 25° C. "Degrees."	Unsaponifiable Matter. Per cent.	Free Fatty Acids. Per cent.
1. Kidney bed after filtration at 13·3° C.	Orange-yellow oil	0·9212	19·63	114·85	0·35	66·7	0·68	...
2. Neck ("mane") after filtration at 12·2° C.	Lemon-yellow oil	0·9182	...	90·10	0·30	61·8	0·46	...
3. Neck ("mane") after filtration at 8·9° C.	Light yellow, part liquid	0·9184	19·56	93·11	0·20	61·8	0·50	1·20
4. Neck fat .	Lemon-yellow oil	0·9211	19·63	112·85	...	66·0	0·42	0·46

The drying properties of horse oil are very marked. Thus specimens of horse oil exposed in thin layers on glass gave at temperatures 95° to 97° C., sticky films after two hours, which became solid after four hours (*Dunlop* [2]).

In consequence of its strong drying power, horse oil is unsuitable for lubricating purposes.

HARE FAT

French—*Graisse de lièvre.* German—*Hasenfett.*
Italian—*Grasso di lepre.*

For tables of characteristics see p. 551.

Hare fat (obtained from several specimens of *Lepus timidus*) is, according to *Amthor* and *Zink*,[3] pale yellow to orange-yellow. It is of soft consistence, and separates on standing into a thick yellow oil and a white crystalline deposit. Even in the fresh state it has a disagreeable rancid smell, which becomes more unpleasant on standing.

[1] *Analyst*, 1907, 318. [2] *Ibid.* [3] *Zeit. f. analyt. Chemie*, 1897, 8.

Physical and Chemical Characteristics of Hare Fat

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Butyro-refractometer. At 40° C	Observer.
15	0·9349	Amthor and Zink	17-23[1]	A. and Z.	35-40[1]	A. and Z.	200·9	A. and Z.	102·2	A. and Z.	1·59	A. and Z.	"Degrees." 49	Drumel
100	0·861	Drumel	28-30	Drumel	44-46	Drumel					Reichert-Meissl Value.			
											2·64	Drumel		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Butyro-refractometer. At 40° C.	Observer.
95·2	Amthor and Zink	0·9361	A. and Z.	36-40[1]	A. and Z.	44-47[1]	A. and Z.	209·0	A. and Z.	93·3	A. and Z.	"Degrees." 36	Drumel
95·5	Drumel			39-41	Drumel	48-50	Drumel						

[1] Capillary tube method.

Exposed to the atmosphere in a thin layer (*e.g.* spread on a glass plate), hare fat dries in about 8 days to a tolerably viscid varnish, becoming solid after 4 more days. The iodine number after 38 days' exposure was 19·4.

Hare fat contains linolic acid (p. 541).

The acid value of the specimen examined by *Amthor* and *Zink* was, in the fresh state, 2·73, and after 6 months, 8.

RABBIT FAT

French—*Graisse de lapin.* German—*Kaninchenfett.*
Italian—*Grasso di coniglio.*

For tables of characteristics see p. 553.

Rabbit fat (from *Lepus cuniculus*) is of a dirty-yellow colour; on standing, it separates into a liquid and a solid portion.

The fat from the wild rabbit differs very notably from that of the tame rabbit in its iodine absorption. On exposure to the atmosphere the fat from the wild animal dries after 7 days to a nearly solid varnish, becoming completely solid after 6 more days. After 50 days' exposure the iodine number was only 26. The fat from the tame animal does not exhibit drying properties.

The acid values of the wild rabbit fat and tame rabbit fat were 7·2 and 6·2 respectively.

As a rule, the fat of domesticated animals is richer in olein than that of wild animals; but in this case, as well as in that of the wild goose, the reverse obtains.

Physical and Chemical Characteristics of Rabbit Fat

Source.	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index.	
	At °C.		Observer.	°C.	Observer.	°C.	Observer.	M'ms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Butyro-refracto-meter. At 40° C.	Observer.
Wild Rabbit	15	0·9393	Amthor and Zink [1]	17-22 [2]	A. and Z.	35-38 [2]	A. and Z.	199·3	A. and Z.	99·8	A. and Z.	0·7	A. and Z.		
Tame Rabbit	15	0·9342	,,	22-24 [2]	,,	40-42 [2]	,,	202·6	,,	67·6	,,	2·8	,,		
												Reichert-Meissl Value.			
	100	0·861	Drumel [3]	28-30	Drumel	44-46	Drumel	..	..	..	..	2·64	Drumel	49	Drumel

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Source.	Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
	Per cent.	Observer.	At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Butyro-refracto-meter. At 40° C.	Observer.
Wild Rabbit .	..	..	0·9246	Amthor and Zink	35-36 [2]	A. and Z.	39-41 [2]	A. and Z.	209·5	A. and Z.	101·1	A. and Z.	"Degrees."	
Tame Rabbit .	..	..	0·9264	,,	37-39 [2]	,,	40-42 [2]	,,	218·1	,,	64·4	,,		
	95·5	Drumel	..	..	39-41	Drumel	48-50	Drumel	..	..	..	..	36	Drumel

[1] *Zeit. f. analyt. Chemie*, 1897, 9. [2] Capillary tube method. [3] *Bulletin de l'Assoc. Belge*, 1896 (9), 323.

(3) Non-drying Animal Fats

HORSE MARROW FAT [1]

French—*Moelle de cheval.* German—*Pferdemarkfett.*
Italian—*Grasso di midollo di cavallo.*

Physical and Chemical Characteristics of Horse Marrow Fat

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.
0·9204-0·9221	24-20 [2]	35-39 [2]	199·7-200	77·6-80·6	1·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.	Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per cent.
0·9182-0·9289	36-34 [2]	42-44 [2]	210·8-217·6	71·8-72·2

Horse marrow fat is pale yellow. A specimen of freshly rendered fat had the acid value 1·0, and a sample three months old 0·8.

GOOSE FAT

French—*Graisse d'oie.* German—*Gänsefett.* Italian—*Grasso d' oca.*

For tables of characteristics see pp. 555, 556.

Goose fat (from *Anser cinereus*) is a semi-pellucid, pale yellow fat of granular structure. It consists of olein, palmitin, stearin, and small quantities of glycerides of volatile acids.

The proportion of soluble fatty acids varies, according to *Young*, from 0·7 to 3·5 per cent, calculated as oleic acid.

There are added in the tables some characteristics of the fat from the wild goose (*Anser ferus*); the iodine value of the latter demonstrates that the fat of the wild goose is richer in olein than that of the domesticated goose.

[1] Zink, *Forschungsberichte über Lebensmittel*, etc., 1896, 441.
[2] Capillary tube method.

Physical and Chemical Characteristics of Goose Fat

	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
	At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.
Domesticated goose	37·8 (water at 37·8=1)	0·909	Young	...	...	...	...	192·6	Valenta
,,	...	...	...	...	...	33-34	Bensemann	184-198	Young
,,	15	0·9229-0·9300	Rözsényi	18·1-18·4	Rözsényi	27·5-31·7	Rözsényi	191·2-193	Rözsényi
,,	15	0·9274	Amthor and Zink	18-20	Amthor and Zink	32-34	Amthor and Zink	193·1	Amthor and Zink
Wild goose . .	...	...	...	18-20	,,	...	...	...	...
Wild goose, 2 years in captivity	15	0·9158	,,	...	...	...	...	196	,,

Physical and Chemical Characteristics of Goose Fat—continued

	Iodine Value.		Reichert-Meissl Value.		Refractive Index. Butyro-refractometer.	
	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 40° C.	Observer.
					" Degrees."	
Domesticated goose	71·5	Erban and Spitzer	...	...	...	...
,,	... 58·7-66·4	Rözsényi	0·2-0·3	Rözsényi	50-50·5	Rözsényi
,,	67·6	Amthor and Zink				
Wild goose . .	99·6	,,				
Wild goose, 2 years in captivity	67·0	,,				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.	
	Per cent.	Observer.	At 15° C.	Observer.	°C.	Observer.	°C.	Observer.
Domesticated goose .	95·88	Bensemann	...	...	...	...	37-38 and 40-41	Bensemann
,, .	92·4-95·7	Young	...	...	...	...	36·6-49·2	Rözsényi
,, .	94·5-95·3	Rözsényi	0·9257	Amthor and Zink	31-32	Amthor and Zink	38-40	Amthor and Zink
Wild goose . .	...	...	...	...	33-34	,,	34-40	,,
Wild goose, 2 years in captivity	...	...	0·9251	,,	32	,,	36-38	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids—continued

	Neutralisation Value.		Iodine Value.	
	Mgrms. KOH.	Observer.	Per cent.	Observer.
Domesticated goose .	...	...	...	...
,, .	...	...	...	...
,, .	202·4	Amthor and Zink	65·3	Amthor and Zink
Wild goose . .	...	...	...	...
Wild goose, 2 years in captivity	196·4	,,	65·1	,,

Adulteration of goose fat with about 20 per cent and more of lard can be ascertained by determining the melting point and solidifying point according to *Polenske's* method (Vol. I. Chap. V.). With pure goose fat differences from 14·7 to 16·7° C. are observed, whereas by the addition of 20 per cent of lard the difference rises to 17·3 and 17·5°, and in the case of an addition of 30 per cent to even 18·3° C.

HUMAN FAT

French—*Graisse d'homme.* German—*Menschenfett.*
Italian—*Grasso d' uomo.*

For tables of characteristics see p. 558.

Human fat was first examined by *Chevreul* and afterwards by *Heintz.*

The consistence of human fat approaches that of butter. On crystallisation from ether *Mitchell*[1] obtained a slight deposit of crystals, melting at 51·5° C.; under the microscope these crystals somewhat resembled those frequently obtained from flare lards. *Partheil* and *Ferié*[2] obtained pure tripalmitin on removing the liquid portion by expression and crystallising the solid portion from absolute alcohol. In the liquid portion dioleo-stearin was identified. Human fat may therefore be considered as consisting chiefly of tripalmitin and dioleo-stearin; neither myristic nor lauric acids were found by the lithium salt method. In the light of these numbers the statement made by *Jaeckle*[3] that the mixed fatty acids consist of 4·9-6·3 per cent of stearic acid, 16·9-21·1 per cent of palmitic acid, and 65·6-86·4 per cent of oleic acid must be accepted with reserve. The amount of unsaponifiable matter was found by *Jaeckle* to be 0·33 per cent; the proportion of lecithin calculated from the phosphorus contents was 0·084 per cent.

The iodine value of the fat of new-born babies was found by *Knöpfelmacher* to be 43·3.[4] The proportion of liquid acids increases, however, rapidly, until at an age of one year the iodine value of 65 (67·25, *Langer*) is found, which is the iodine value of the fat from adults. (In the case of young pigs *König* and *Schluckebier*[5] ascertained that the iodine value decreases with the age, and that the melting point of the fat increases correspondingly.) The fat of well-fed children is richer in oleic acid than that of underfed ones. The influence of food on the iodine value of the fat is further clearly illustrated by the statement made by *Rosenfeld*[6] that the fat of Polynesians, living chiefly on cocoa nuts, resembled somewhat

[1] *Analyst*, 1896, 172. [2] *Archiv d. Pharmacie*, 1893, 545.
[3] *Chem. Zeit.* 1897, 163. [4] *Chem. Centr.* 1898, i. 788.
[5] *Zeit. f. Unters. d. Nahrungs- u. Genussm.* 1908, 641.
[6] *Chem. Zeit.* 1902, 1110.

Physical and Chemical Characteristics of Human Fat

	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Thermal Test.		Refractive Index. Butyro-refracto-meter.	
	At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Heat of Bromination. ° C.	Observer.	At 40° C.	Observer.
																"Degrees."	
Adult	15	0·9179	Jaeckle [1]					193·3-199	Jaeckle			0·25-0·55	Jaeckle				
	25 (water 25° = 1)	0·9033	Mitchell [2]	15	Mitchell	17·5	Mitchell	195 196·25-198·1	Mitchell Partheil and Ferié	61·5 57·21-66·31	Mitchell Partheil and Ferié	0·5 1·12-2·12	Mitchell Partheil and Ferié	11·3	Mitchell	49·6-53	Mitchell
New-born babies								204·3	Jaeckle	47·3-58·1	Jaeckle	1·75-3·4	Jaeckle				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.	Melting Point.	Iodine Value.	Observer.
Per cent.	Observer.	° C.	° C.	Per cent.	
95·3	Kretschman	30·5	35·5	64	Mitchell
93·92-96	Partheil and Ferié				
				Iodine Value of the Liquid Fatty Acids.	
				92·1	,,

[1] *Chem. Zeit.* 1897, 163.

[2] *Analyst*, 1896, 172.

cocoa nut oil, whereas the fat obtained from an Eskimo had the iodine value 79—thus showing the influence of the blubber oil taken in the food.

The variations in the chemical characteristics of fat from the various parts of the human body do not interest us here, and the reader must, therefore, be referred to the footnotes. The following statement, if read in conjunction with the remarks made on p. 544, may, however, prove interesting. The fat taken from the muscles of the heart of a person who had been suffering from fatty degeneration of the heart, gave the following numbers [1]:—

Saponification value	257·4
Iodine value	108·55
Reichert-Meissl value	23·9
Acid value	18·35

According to *P. Hartley* [2] the higher fatty acids from the *liver*, *kidney*, and *heart-muscle* include, in addition to saturated acids and acids of the oleic series, considerable amounts of acids of the series $C_nH_{an-4}O_2$, $C_nH_{2n-6}O_2$, and possibly $C_nH_{2n-8}O_2$. These unsaturated fatty acids yield on bromination additive products insoluble in ether, carbon tetrachloride, alcohol, and acetic acid, thus resembling the bromo-acids of the series $C_nH_{2n-8}O_2$.

Fat extracted from human hair (*Meyer* [3]) had the following characteristics:—

Specific gravity at 60° C.	0·9086
Saponification value	200
Iodine value	67
Reichert-Meissl value	2·3
Insoluble fatty acids + unsaponifiable	90 per cent
Unsaponifiable matter	3 per cent
Refractive index at 28° C.	1·47009

When decomposition of the human body sets in, the tissue disappears first, and the more resistant fat is converted into the so-called *adipocere* (French, *Adipocire*; German, *Leichenwachs*; Italian, *Cera cadaverica*), a hard wax-like mass consisting chiefly of fatty acids (cp. Vol. I. Chap. I.) and lime soaps of fatty acids.

Adipocere was first described by *Antoine François Fourcroy*, who placed it together with cholesterol (found by *Conrad* in 1775 and by *Green* in 1788 in the biliary calculi) and spermaceti in a separate class termed "adipocere." *Schmelck* [4] examined three specimens of adipocere, with the following result:—Melting point, 62·5° C.; insoluble fatty acids, 83-84 per cent; ash, 1·64-1·79 per cent (containing 83-84 per cent CaO); unsaponifiable matter, 16·7 per cent; acid value, 197; neutralisation value of the fatty acids, 202·8-203·4; iodine value, 14-14·2; iodine value of the fatty acids,

[1] Lindemann, *Zeit. f. Biol.* 1899, 38; 405.
[2] *J. Physiol.* 1907 (36), 17.
[3] *Chem. Zeit.* 1905, 1028.
[4] *Ibid.* 1902, 11.

14·4. According to *Tarugi*,[1] adipocere consists chiefly of palmitic acid.

With regard to fat obtained from Egyptian mummies, cp. *W. A. Schmidt*.[2]

LARD, HOG FAT

French—*Saindoux, Graisse de porc.* German—*Schweinefett.* Italian—*Strutto.*

For tables of characteristics see pp. 565-567.

"Lard" originally used to denote the fat rendered from the leaf of the pig, *i.e.* the fat from the kidneys and the bowels.

The increased consumption of lard during the latter half of the last century (which has seen the rise of large American packing houses manufacturing lard on an enormous scale) has chiefly contributed to the extension of the above given definition of lard, so that at present *lard* denotes the fat from any and every part of the hog.

What was originally termed lard is still being sold on a small scale as "butcher's lard" and "home-rendered lard." Compared with the enormous quantities which are being produced in the slaughter-houses of America, especially in those of the United States, the amount of lard which is produced locally on a small scale has become an insignificant quantity. That produced in large municipal or private slaughter-houses no longer consists entirely of leaf lard. "Bladder lard"—so named from the package—used to be leaf lard rendered in small establishments. This term is still used to denote the best quality of home rendered, as also of American lard of quality (*c*) (see below). Another quality of lard, sold in the retail trade as "keg lard" (so named from the package), always contains, besides leaf lard, the fat taken from other parts of the animal.

As stated already, at present "lard" denotes the fat taken from any and every part of the hog. Implicitly this has been recently acknowledged by the Adulteration Laws of the United States, according to which the term lard is defined as the "rendered fat from slaughtered, healthy[3] hogs free from rancidity and containing no more than 1 per cent of substances other than hog fat." The production of, and trade in, lard made at present may be considered as being completely dominated by the processes and trade usages in vogue in the United States, especially in the large packing houses of Chicago.

[1] *Gazz. chim. ital.* 34, ii. 469; *Chem. Centr.* 1905, i. 683. The statement that adipocere consists chiefly of palmitic acid was first made many years ago (Wetherill, *Trans. Amer. Philos. Soc.*). Cp. also E. Salkowski, *Zur Kenntniss der Fettwachsbildung*, p. 20 (Festschrift f. R. Virchow, 1891, Berlin, Reimer).

[2] *Chem. Zeit.* 1908, 769.

[3] This is important, as in the State of Iowa a law is in force which says that lard made from hogs that have died of disease may be sold if the fact be mentioned to the purchaser at the time of sale.

The rules of the Chicago Board of Trade define the following brands of edible lard:—(*a*) *Neutral Lard No.* 1; (*b*) *Neutral Lard No.* 2 (*Imitation Neutral Lard*); (*c*) *Leaf Lard*; (*d*) *Choice Lard, Choice Kettle-rendered Lard*; (*e*) *Prime Steam Lard.* These brands will be described here in the order in which they are produced, so as to give, at the same time, a concise account of the manufacturing processes involved in the production of edible lard.

In the American packing-houses, in some of which up to 10,000 hogs are killed per day, the animals are driven into a shackling pen, where they are fastened to a "wheel hog hoist" by means of which they are hoisted up to the "sticking-pen." Immediately after they have been killed they are delivered automatically by a travelling band into a "scalding tub," from which the carcases are thrown out and carried automatically into the hog-scraping machine, where the bristles are scraped off. The carcases are then cut up immediately, and in the first instance the leaf (French—*panne*; German—*Liesen, Flohmen*; Italian—*sugna*) is taken out, freed from the flesh and skin, and then chopped up in fat-cutting machines into small lumps and thoroughly washed with iced water. The comminuted mass is then delivered into jacketed rendering vessels, in which it is heated up to a temperature of 40° to 50° C. The lard so obtained—(*a*) *Neutral Lard No.* 1—is practically neutral, and is used almost exclusively in the manufacture of "margarine" (termed in America "oleo-margarine").

If the leaf cannot be rendered in its fresh state, it is placed in refrigerating rooms until it can be worked up. The first method can, of course, only be used in small establishments, whereas the latter method, as the author has himself seen in the Chicago stock-yards, is the one practised on a large scale. Moreover, it is claimed that the so-called "animal flavour" is more efficiently removed by a prolonged cooling process.

The fat from the back[1] is rendered in a similar manner. The skin is either removed by hand or by a back-fat skinning machine. This lard is sold as (*b*) *Neutral Lard No.* 2, "Imitation Neutral Lard" (quoted on the Rotterdam Exchange as "Imitation lard"). This fat is used in America chiefly for the purposes of confectioners and biscuit bakers. On the continent of Europe this lard finds extensive use for the same purposes, further in the manufacture of margarine, and also as an adulterant of butter (see "Butter Fat").

Neutral lard No. 1 and Neutral lard No. 2 (not being "cooked") do not keep well and cannot, therefore, be used like "leaf lard" and "steam lard" for domestic purposes. The author would explain this fact as being due to the enzymes (which he considers as the primary cause of the incipient stages of rancidity) not having been destroyed

[1] The back-fat lard is separated by a fascie into two layers, the outer one of which melts at a lower temperature than the inner. This peculiarity extends even so far that hogs reared in colder climates have a considerably softer (that is, richer in olein) outer fat layer than the hogs reared in warmer climates. Such differences are not noticeable in the fat of the inner portions of the body.

completely at the comparatively low temperature at which these two brands of lard are rendered.

(*c*) *Leaf Lard* (German—*Speckschmalz*).—On subjecting the residue from (*a*) to steam heat under pressure in autoclaves, the leaf lard of commerce is obtained. Formerly this was the only kind of lard recognised by the Chicago Board of Trade, and was then prepared from the whole leaf, and thus embraced the three qualities described under (*a*), (*b*), and (*c*). This lard is not exported, but is consumed at home. The Adulteration Laws of the United States now define *leaf lard* as "the lard made from the internal fat of the abdomen, excluding that adhering to the intestines, and having the iodine number 60." The "cracklings" from best leaf-lard are mixed with bone meal and sold as chicken food under the name of "azotine."

The portions of the leaf remaining after the rendering of *Neutral Lard No.* 1 are frequently put together with the residues obtained in the preparation of *Neutral Lard No.* 2 and rendered by steam heat either in open steam-jacketed kettles or in autoclaves. The lard so obtained consists, therefore, exclusively of the residue from *Neutral Lard No.* 2 or from a mixture of residues from *Neutral Lard No.* 1 and *Neutral Lard No.* 2. This lard is known as (*d*) *Choice Lard*, *Choice Kettle-rendered Lard* (French—*Saindoux de choix*). The open steam-jacketed kettles are a survival of the old-fashioned open kettle, in which butchers used to render the lard over free fire. Such lard had the peculiar, pleasant flavour of fried fat, and therefore the name "kettle-rendered lard" has been retained even after the rendering over free fire had given way to heating by means of steam. In large establishments the rendering is carried out under pressure (in autoclaves). In some establishments, however, the jacketed vessels are still in vogue; they are usually square tanks, provided with one or more circular flue-pipes passing through the centre of the tank, so as to distribute the steam over as large a surface as possible. According to the regulations of the Chicago Board of Trade, "choice lard" is defined as lard made from leaf and trimmings only, either steam or kettle-rendered; the manner of rendering must be branded on each tierce. Its flavour is much superior to that of "prime steam lard."

After this lard has been drawn off from the autoclave, the residue termed "tankage" is withdrawn and worked up in the fertiliser department (see Chap. XVI.).

The lowest quality of edible lard is (*e*) *Prime Steam Lard* (French—*Saindoux à la vapeur*; German—*Dampfschmalz*), also termed "standard prime steam lard," and obtained from any trimmings not used up in the production of lard (*d*), and all other parts of the hog that will yield lard, with the exception of the liver, lungs, the intestines proper, of that part of the heart which is free from fat, etc. This quality is rendered in autoclaves in a similar manner to (*d*). This lard is passed solely on inspection, and as the inspector has no authority enabling him to supervise rendering establishments, in order to

secure a proper control, we may take it that prime steam lard consists of the fat from any part of the hog, either from the whole animal or from portions of it (head, foot).

As stated already, these qualities are used for edible purposes only.

All those parts of the hog which have not been used for the production of edible lard — such as "guts," etc.—are worked up in autoclaves, in order to obtain the last portions of fat they contain. Such fat is known as "yellow grease" (see Chap. XVI.). With it is mixed all the refuse fat resulting in the course of rendering the edible qualities. The "yellow grease" is generally worked up together with any hogs that have died in the "Stock-yards." This quality is, of course, only used for manufacturing purposes, such as for the production of soap, low quality lard oil, or "grease stearine."

The hogs which have died in transit are rendered for fat in their entirety, after the intestines have been removed, as the fat from the latter would discolour the resulting grease. The grease so obtained is sold as "white grease" for manufacturing purposes.

The intestines which have been removed from the dead animals are worked up separately, and yield a grease sold as "brown grease." This is used for the manufacture of soaps and the lowest class of commercial lard oil.

A further kind of grease—"pig's foot grease"—is a by-product obtained in the glue department of the packing houses. It also finds an outlet in the manufacture of low-class lard oil and of soap.

In this section only lard proper will be dealt with, *i.e.* all the edible qualities enumerated above from (*a*) to (*e*) (cp. Vol. III. Chap. XVI. "Greases").

The two qualities of "neutral lard" hardly require any refining. After the clear melted lard has settled in the jacketed vessel, it is run off into a receiving tank, in which the last traces of water and any fibres are precipitated by sprinkling salt over the fat (cp. manufacture of "Premier Jus," Chap. XV.). The settled lard is then ready for use in the margarine department of the works, or is run into tierces for shipment.

The next qualities of edible lard usually undergo a more complicated process of refining. This consists in treating the melted fat in a refining vessel with fuller's earth, blowing it at the same time with air. This is done not only to mix the lard but also to deodorise those qualities which require such treatment. The treated mass is then pumped through a filter-press, from which the clear, bleached lard is run over horizontal cylinders cooled by brine. In small establishments a single cooler is used; in the large packing-houses two cooling cylinders, arranged side by side in one open tank, are usually employed. These cylinders revolve slowly in the warm lard, being immersed in it to about half their diameter. Whilst rotating they carry up a layer of lard, which is quickly chilled on the cooled surface

and forms a continuous sheet of solidified fat. On the opposite side, before the cylinder dips again into the warm lard the solidified mass is removed by a scraper, and falls into a trough. In this trough a rotating screw conveyer breaks up the sheet of fat and carries it forward into a mixer, in which the lard is agitated by a mechanical arrangement. Here lard stearine is added, if need be, to "stiffen" soft lard.

At this stage of the process such ingredients as are incorporated with lard in the manufacture of "Lard substitutes" (see Chap. XV.) are also added.

The finished product is taken off by a pump, which delivers the semi-solid mass through a range of strainers into the vessels ("tierces") in which the lard is shipped.

The object of the agitation of the lard is to produce rapid solidification of the mass, whereby a whiter product is obtained than if the lard were allowed to solidify slowly. Frequently the lard is blown at the same time with air, which becoming entangled during the agitation assists in giving a whiter colour to the lard. This final treatment in the agitator imparts the smooth, salve-like consistence, and also prevents the formation of crevices in the finished product which not only render the lard unsightly, but also increase the liability to rancidity by the more ready access of air. The mixing in the agitator and the blowing with air require careful observation. If not carried to a certain point, liquid portions would separate out in the tierces. The author has not infrequently noticed pools of fluid fat in tierces containing lard of a low melting point.

The machinery used in the large American packing houses has served as a type to those European establishments where considerable quantities of lard are produced (*e.g.* in Vienna). Slight alterations are introduced into the system of cooling, as the quantities produced are not always large enough to permit the installation of brine-cooled cylinders. In such cases the hot lard is worked off in mixing machines between rollers where lard in solid form is introduced in order to induce more rapid solidification, or even lard stearine to "stiffen" the lard. Just as in the manufacture of lubricating greases and vegetable butters, the object of passing the lard between rollers is to give it a smooth appearance. With regard to the manufacture of "Lard Stearine" and "Lard Oil" see p. 614.

Reliable figures representing the extension of the lard trade in the United States of America, Canada, etc., are not available, but some information may be gathered from the following data:— In the year 1899 the quantity of neutral lard consumed in the production of margarine (oleomargarine) amounted to 31,297,251 lbs. In addition to this there is the consumption of lard in the United States and the amount used in the production of lard compounds (see Chap. XV. "Lard Substitutes"). The bulk of the lard is, however, exported to Europe.

Physical and Chemical Characteristics of Lard

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·934-0·938	Dieterich	27·1-29·9	Goske	42-48	Koenigs	195·3-196·6	Valenta
40 (water at 15·5=1)	0·8985	Allen			45-46	Bensemann	195·2-196·2	Lewkowitsch
					36-45·5	Dieterich		
50 (water at 50=1)	0·89159-0·90038	Fairley and Cooke			(Cp. p. 580)	Lewkowitsch		
90	0·894-0·897	Dieterich			,, ,,	Dunlop		
98-99 (water at 15·5=1)	0·8608	Allen						
100 (water at 15=1)	0·861	Koenigs						
100	0·8610-0·8614	Gladding						
100 (water at 15=1)	0·8589-0·8641 [1] (American)	Dennstedt and Voigtländer						
			Fat from	*Wild Boar*				
15	0·9424	Amthor and Zink	22-23	Amthor and Zink	40-44	Amthor and Zink	195·1	Amthor and Zink
			27·9-30·8 [3]	Richardson [2]	32-37·5 [3]	Richardson		
			24·7-27·3 [4]	,,	32 [4]	,,		

[1] In one case 0·8700 was found. [2] *Journ. Amer. Chem. Soc.* 1904, 372. [3] From leaf. [4] From back.

Physical and Chemical Characteristics of Lard—continued

Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.			At 60° C.	Observer.
49·9-63·8	Dieterich	0·49-0·77	Fendler	(See Table, p. 586.)		1·4539	Thoerner
62·4 (American)	Schweitzer and Lungwitz					Oleo-refractometer.	
60·4-70·4 (American)	Raumer						
59-68·4 (American)	Dennstedt and Voigtländer					"Degrees."	Observer.
55 (European)	,,					−12·5	Jean
53-76·9	Lewkowitsch						
58·1-85 (Chinese)	Farnsteiner					Butyro-refractometer.	
(Cp. also pp. 582-584.)					At °C.	"Degrees."	Observer.
					25	56·8-58·5	Spaeth
	Fat from Wild Boar				40	50-51·2	Benedikt and Wolfbauer
					,,	48·6-51·2	Mansfeld
76·6	Amthor and Zink	0·68 (R.)	Amthor and Zink		,,	44·8-53	Dennstedt and Voigtländer
					,,	48·1-50·7	Dunlop [3]
78·8-82 [1]	Richardson				,,	53·3-54·2	Farnsteiner [4]
81·5-84·7 [2]	,,				,,	53·8-57·3	,, [5]

[1] From leaf. [2] From back. [3] Fats from different parts of the body ; cp. *Journ. Soc. Chem. Ind.* 1906, 458.
[4] Chinese lards. [5] Japanese lards.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.			Specific Gravity.			Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
Per cent.	Observer.		° C.		Observer.	° C.	Observer.	° C.	Observer.		Observer.	Per cent.	Observer.	° C.	Observer.	At 60° C.	Observer.
95·8	Bensemann		99° (water 15·5 = 1)	0·837-0·840	Allen	34 39 39 41·45-42 (Titer test) 36·0 [2]	Mayer Allen Terreil Lewkowitsch ,,	35 44 43 43-44 and 46-47	Mayer Allen Terreil Bensemann	278	Allen	64·2	Williams	10·4-11	Hehner and Mitchell	1·4395	Thoerner.
												Iodine Value of the Liquid Fatty Acids.				Oleo-refractometer.	
												89·4-90·7 (European)	Dieterich			"Degrees."	Observer.
												93-96 (European)	Wallenstein and Finck			−30	Jean
												103-105 (American)	v. Raumer			Butyro-refractometer. (See p. 587.)	
												96·9-103·2 (American)	Bömer				
												93·5-103·7 (European)	,,			Refractive Index of the Liquid Fatty Acids.	
												95·2-104·9 (American)	Lewkowitsch				
												92-115·5 [2] (European-American)	Tortelli and Ruggeri			Butyro-refractometer.	
												97·0 [3]	Farnsteiner			At 40° C.	Observer.
												99·8 [4]	,,			43·1-44·7	Bömer
												113-121·7 (Chinese)				44-45	Mansfeld
												124·2-138·7 (Japanese)					
												Fatty Acids.					
		Wild boar	15	0·9333	Amthor and Zink	32·5-33·5	Amthor and Zink	39-40	Amthor and Zink	275·5 [1]	Amthor and Zink	81·2	Amthor and Zink				

[1] Calculated from saponific. value 203·6. [2] Iodine value of lard 76·9. [3] Genovese lard of iodine value 57·5. [4] Iodine value of lard 63·2.

The exports of lard from the United States in lbs., and their value in dollars, is given in the following table :—

Year.	Lbs.	Dollars.
1896	509,534,256	33,589,851
1897	568,315,640	29,126,485
1898	709,344,045	39,710,672
1899	711,259,851	42,208,465
1900	661,813,663	41,939,164
1901	611,357,514	46,560,148
1902	556,840,222	52,375,864
1903	490,755,821	50,854,504
1904	561,302,643	46,347,520
1905	610,238,899	47,243,181
1906	741,516,886	60,132,091
1907	...	57,497,980

The quantity of "lard compounds" and "lard substitutes" exported from the United States will be given in Chapter XV. under the heading "Lard Substitutes."

The following figures state the value in £ of the imports into, and the re-exports from, the United Kingdom of lard and imitation lard (see above), and also of "lard substitutes" :—

[TABLE

Imports of	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
	£	£	£	£	£	£	£	£	£	£
Lard . . .	2,887,801	3,068,975	3,266,582	4,037,689	4,118,992	3,870,774	3,342,389	3,692,573	4,361,399	4,491,539
"Imitation Lard"[1].	89,025	90,010	98,629	154,239	284,830	306,633	238,668	269,098	358,492	408,192
Re-Exports of										
Lard . . .	674,828	810,903	480,797	551,512	155,457	189,982	194,159	419,257	401,743	379,481
"Imitation Lard" .	11,875	4,332	2,276	1,453	6,548	1,202	1,652	4,005	8,500	5,805

[1] This term including besides "neutral imitation lard" (see above) also lard substitutes.

Very large quantities are shipped to the French ports; and to Rotterdam, which is the chief port for the importation of lard into Germany.

A reliable estimate as to the European production is at present impossible. The author, from information placed at his disposal, estimated that the value of lard produced in the United Kingdom was about £1,100,000 in 1902. Large quantities of lard are produced on the Continent in Roumania, Servia, Hungary, and Austria. Hardly any lard can be imported into Hungary and Austria in consequence of the enormous import duty on this article.

Leaf lard has a granular texture and a salve-like consistence, and should be of pure white colour. The lards which represent mixtures from all parts of the body, especially those manufactured in large slaughter houses, have no longer a crystalline texture, as the object of the last operation in the manufacture is to destroy such texture and give to the produce a smooth appearance.

The lard rendered from the leaf and also that from the back have an agreeable taste. The lower qualities have an insipid taste; this disappears, however, on standing. Some of the steam lards have an "animal flavour," which may be judged by an inexperienced person as indicating admixture with tallow or beef "stearine." This flavour also disappears on standing or on warming.

Leaf lard is the hardest; the lards from the back, etc., are softer (see below under "Melting point," p. 579). The consistence of a lard is not only conditioned by the part of the animal from which it has been taken, but depends also on the food which has been given to the animal. Hogs fed exclusively on acorns yield a harder lard than hogs fed on maize.

Lard consists of the glycerides of lauric, myristic, palmitic, stearic, and oleic acids, and small quantities of linolic acid (and perhaps also of linolenic acid). The proportion of stearic acid in a number of commercial lards (determined by the method described, Vol. I. Chap. VIII.) varied from 6 to 24·91 per cent. The statement made first by *Fahrion*, viz. that lard contains linolic acid, is confirmed by the fact that the liquid fatty acids of lard, especially of American lards, have iodine values varying from 93-106, and reach even 115·5, as I have ascertained recently. "Daturic" acid, stated by *Kreis* and *Hafner* to occur in lard as a mixed glyceride "daturodistearin," has been shown to consist of a mixture of solid acids (see below).

[TABLE

Farnsteiner found in a specimen of European lard (of the iodine value 51·4) the following percentages of solid and liquid acids[1] :—

	Solid Fatty Acids.	Liquid Fatty Acids.
	Per cent.	Per cent.
Lard I. (iod. val. 51·4) .	41·3	53·7 (iod. val. 93)
,, II. . . .	42·2	53·1

[1] Lard derived from "oily hogs" differs from ordinary lard, as is shown by the following table, due to Richardson and Farey (*Journ. Amer. Chem. Soc.* 1908, 1911) :—

Kind of Fat.	Fat.					Insoluble Fatty Acids.					
	Melting Point.		Saponification Value.	Iodine Value.[1]	Refractive Index.	Free Acid (as Oleic). Per cent.	Melting Point (Titer Test). °C.	Liquid Fatty Acids. Per cent.		Iodine Value.[1]	Refractive Index.	Bromides insoluble in Petroleum Ether at 8° C. Per cent.
	Open Capillary Tube, lower limit. °C.	Closed Capillary Tube, upper limit, completely clear. °C.			At 40° C.			Calculated to Fat.	Calculated to Fatty Acids.		At 60° C.	
Back fat .	−1·5	12·0	189·0	93·9	1·4620	0·16	21·2	84·4	89·4	104·5	1·4452	. .
Leaf lard .	−1·6	17·0	191·0	95·2	1·4620	0·16	21·6	84·2	89·2	106·8	1·4452	. .
Leaf lard .	−0·8	22·0	192·5	92·6	1·4621	0·26	23·8	81·5	86·3	110·0	1·4453	. .
Leaf lard .	+0·9	21·0	190·5	93·8	1·4621	0·14	23·4	82·9	87·8	106·9	1·4448	. .
Ham fat .	0·0	18·0	189·0	92·8	1·4620	0·20	21·8	82·2	87·1	108·3	1·4450	1·51[2]
Ham fat .	−2·4	13·0	190·5	95·1	1·4640	0·16	19·3	81·1	85·9	109·7	1·4455	. .

[1] Determined with iodine bromide.

[2] Not obtained in a crystalline condition.

The 53·1 parts of liquid fatty acids of specimen II. were resolved by the barium-salt-benzene method into 39·2 parts of oleic acid and 13·9 parts of less saturated acids. The presence of linolic acid was proved by the isolation of linolic tetrabromide. Since a brominated acid of the melting point 165° C. was isolated, the inference is justified that this product represents a mixture of linolic tetrabromide and linolenic hexabromide.

Twitchell[1] calculated the composition of a lard (iodine value of the mixed fatty acids = 62·57) as follows :—

	Per cent.
Linolic acid	10·06
Oleic acid	49·39
Solid acids (difference)	40·55

The iodine values of the two fractions of liquid acids he prepared were 109·35 and 118·02.

The composition of an American lard, absorbing 65·78 per cent of iodine, was examined by *Partheil* and *Ferié*,[2] by their lithium salt method. The analysis detailed in the third edition of this work (p. 780) is not reproduced here, as the correctness of the method is open to doubt.

On treating lard with 95 per cent alcohol some glycerides richer in olein than the bulk pass into the alcohol. As this behaviour is of importance for the detection of more readily alcohol-soluble oils and fats (such as cocoa nut oil) in lard (cp. p. 600), the results of several experiments made by *Arnold*[3] are appended. 150 grams of lard were heated with 1100 c.c. of 95 per cent alcohol for an hour on the water bath under a reflux condenser, and the mass then allowed to stand for 4-5 hours at 12-14° C. In the following table some characteristics of (I.) the original lard, (II.) the alcohol-soluble portion, and (III.) the alcohol-insoluble portion are collated :—

[1] *Journ. Soc. Chem. Ind.* 1895, 515 ; cp. 2nd edition of this work, p. 567.
[2] *Arch. d. Pharm.* 1903, 566.
[3] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1907, xiv. 179.

[TABLE

	Butyro-refractometer at 40 °C. "Degrees."	Saponification Value.	Reichert-Meissl Value.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids. Polenske's method.	Iodine Value.	Insoluble Fatty Acids.			Yielded Alcohol-soluble portion.
						Butyro-refractometer at 40° C. "Degrees."	Neutralisation Value.	Iodine Value.	
American Lard									
I. Original Lard . .	50·1	194·9	0·33	0·55	62·5	36·7	204·4	64·2	...
II. Alcohol-soluble Fat .	52·7	190·5	0·66	0·55	68·0	40·6	200·1	73·4	9·1 g.
III. Alcohol-insoluble Fat	50·6	196·0	0·44	0·50	60·4	37·0	205·0	62·0	...
German Lard									
I. Original Lard . .	47·7	193·8	0·55	0·50	49·0	34·5	202·3	50·9	...
II. Alcohol-soluble Fat .	49·2	189·9	0·88	0·70	63·9	38·0	200·4	66·1	6·9 g.
III. Alcohol-insoluble Fat	47·8	196·0	0·65	0·55	47·8	34·0	203·8	49·4	...
German Lard									
I. Original Lard . .	48·4	195·7	0·44	0·60	53·2	34·1	204·3	53·9	...
II. Alcohol-soluble Fat .	51·4	191·5	0·88	0·75	66·1	38·9	200·6	67·2	6·4 g.
III. Alcohol-insoluble Fat	48·3	196·1	0·55	0·55	51·7	33·7	203·9	52·2	...

The analytical differences between lards from different parts of the hog are summarised in the following tables. Since important differences exist between North American and European lards, owing to the modes of fattening, I consider it useful to differentiate as far as possible between European and American lards.

European Lards

Fat from	Spec. Grav. at 100° C. (Water 15=1.)	Melting Point of Fat.	Melting Point of Fatty Acids.	Iodine Value of		Free Fatty Acids.		Observer.	Remarks.
				Fat.	Fatty Acids.	c.c. norm. KOH per 100 grms.	Calculated to Oleic Acid.		
		°C.	°C.				Per cent.		
Back .	0·8607	33·8	40	60·58	61·90	0·54	0·152	Spaeth	Mean results from examination of fats from 8 animals.
Kidney .	0·8590	43·2	43·2	52·60	54·20	0·58	0·163	,,	
Leaf .	0·8588	44·5	42·9	53·10	54·40	1·28	0·360	,,	

North American Lards

Fat from	Specific Gravity at 100° C. (Water at 15° C. = 1.)	Iodine Value.	Maumené Test from 40° C.	Melting Point (Bensemann's Method).		Refractive Index.	Observer.
				Drop formed at °C.	Melted to a clear drop. °C.	Butyro-refractometer at 40° C.	
			°C.			"Degrees."	
Head	0·8637	66·2	33	24	44·8	52·6	Dennstedt and Voigtländer
	0·8629	66·6	32	24	44·8	52·5	
	0·8631	65·0	34	24	45·0	52·0	
Back	0·8611	61·5	37	28·5	48·5	52·4	
	0·8621	65·0	35	28·5	48·5	51·8	
	0·8616	65·1	38	31·5	46·0	51·9	
Leaf	0·8637	62·2	...	26	45	51·4	
	0·8615	59·0	...	29	44	50·2	
	0·8700	63·0	30	28·5	44·5	52·0	
Foot (hoof)	0·8589	68·8	...	24	40	44·8	
Ham	0·8641	68·4	38	26	45	51·9	
	0·8615	66·6	...	26	44	51·9	
	0·8628	68·3	...	26	44·5	53·0	
Ham (German)	0·8597	55·0	30	32	46	49·2	Dennstedt and Voigtländer

As a corollary I add the following table, setting out the percentages of stearic acid in lards taken from different parts of a hog :—

Fat from	Melting Point. °C.	Iodine Absorption.	Stearic Acid.		Observer
			Per cent.	Melting Point. °C.	
Head .	34·8	67·7	8·67-9·47	67·8-66·2	Hehner and Mitchell
Ham .	34·6	61·6	8·74-9·02	67·5-67·3	,, ,,
Breast .	36·8	64·2	11·84-10·9	67·2-66·8	,, ,,
Flare .	40·0	52·8	15·7-14·4	66·5-67·2	,, ,,
Back .	35·6	67·9	8·59-9·2	67-66·5	,, ,,
Kidney bed	50	53·4	19·2	...	Dunlop
?	37-40	58·6	22·3	...	Kreis and Hafner
?	...	45·6	24·9	...	Hehner

Pure lard contains small quantities of unsaponifiable matter. *Allen* and *Thomson* found 0·23 per cent, *Lewkowitsch* 0·35 per cent. The bulk of the unsaponifiable matter consists of cholesterol. It should be noted that the cholesterol can be readily obtained in well-formed crystals. As to the importance of the amount of unsaponifiable matter in the examination of lard for adulterants, see below, p. 590.

Freshly rendered lard is practically neutral ; determinations made by several chemists of the free fatty acids gave the following numbers :—

Free Fatty Acids as Oleic Acid.	No. of Samples.	Observer.
Per cent.		
0·280-0·420	?	Dieterich
0·350-1·000	12	Wiley
0·098-0·564	24	Spaeth

The increase of acidity on exposure to air in loosely corked flasks is numerically shown in the following table, together with the fluctuations in the iodine number (*Spaeth*) :—

[TABLE

No.	Free Fatty Acids; c.c. norm. KOH per 100 grms.			Iodine Value.			
	Freshly rendered.	After one year.	After three years.	Freshly rendered.	After one year.	After three years.	
						Fat.	Liquid Fatty Acids.
1	0·6	6·4	32·0	63·25	53·80	39·26	74·51
2	0·45	2·75	23·0	61·15	55·45	39·37	74·60
3	0·75	7·80	31·6	62·90	51·85	39·56	72·48
4	0·80	11·60	50·0 [1]	62·95	48·80	29·41	
5	1·25	6·70	36·0	57·25	49·40	26·51	64·30
6	0·35	6·00	30·0	55·88	47·80	31·19	
7	0·45	8·40	23·0	60·10	51·04	41·08	69·20
8	0·55	21·20	41·3	55·80	37·50	22·97	
9	1·45	1·80	10·0	52·30	52·20	40·91	
10	0·55	9·60	30·0	57·08	46·70	33·69	
11	1·60	15·40	46·0	51·75	36·71	21·56	
12	0·65	9·60	33·0	63·61	49·00	38·04	
13	0·60	4·20	18·0	52·35	46·85	36·48	
14	0·50	7·60	32·0	60·95	52·72	36·03	

The free fatty acids were separated into soluble and insoluble acids by washing the lards with hot water. Their relative proportions were measured by the amounts of normal alkali required to saturate the free acids. The following table gives the details:—

No.	Free Fatty Acids after three years' exposure.	Soluble Fatty Acids.	Insoluble Fatty Acids.[2]
	c.c. normal Alkali per 100 grms.	c.c. normal Alkali per 100 grms.	c.c. normal Alkali per 100 grms.
1	32·0	4·5	27·5
2	23·0	4·7	18·3
3	31·6	4·2	27·4
4	50·0	8·1	41·9
5	36·0	6·6	29·6
6	30·0	4·0	26·0
7	23·0	3·4	29·6
8	41·3	7·4	33·9
9	10·0	1·9	8·1
10	30·0	3·9	26·1
11	46·0	7·1	38·9
12	33·0	4·1	28·9
13	18·0	2·1	15·9
14	32·0	4·4	27·6

Lard (like butter and olive oil) used to be adulterated on the largest scale. Beef fat, beef stearine, cotton seed oil, cotton seed stearine, and other vegetable oils were the adulterants most frequently employed. In the United States of America admixture with

[1] Corresponding to 14 per cent of oleic acid.
[2] Evidently found by difference.

foreign fats and oils had become an openly acknowledged practice, nay, it had even been claimed that the addition of cotton seed oil constituted an improvement in the manufacture. Thus the American brand "refined lard" was found to be a mixture of lard with cotton seed oil, and a sufficient quantity of beef stearine to obtain the consistence possessed by pure lard. Owing to the interference of the law in this and in other countries, the name "refined lard" has been abandoned, and has been replaced by such terms as "compound lard" or "lard compound." Some of these artificial preparations did not even contain any lard at all, being judiciously prepared mixtures of beef stearine and cotton seed oil or cotton seed stearine. These are now sold as "lardless beef" and under a variety of other fancy names (see Vol. III. Chap. XV. "Lard Substitutes").

Water, which was often used as an acknowledged admixture, is not common at any rate in American lards imported into Europe. Adulteration of this kind may be practised on a small scale, but is of little importance commercially. It may, however, be stated that in some countries, lard containing water is demanded by the buyer. Thus for export to Cuba, lard is prepared which contains 25 per cent of water. In this case water cannot be looked upon as an adulterant as the admixture is openly acknowledged. Lard so prepared was sold a few years ago in Europe as a butter adulterant under the name of "lardine."

Recently *Polenske*[1] ascertained that lard dissolves about 0·45 per cent of water at 96° C., and 0·15 per cent at 42° (which may be looked upon as the average melting point of lards); in both cases transparent liquids were obtained. If a larger quantity of water be present, the lard is no longer able to hold it in solution, and forms then, according to the proportion of water present, either a turbid liquid or two layers, water separating out as a lower layer. Larger amounts of water than those stated above must be considered as not permissible. (*Polenske* determines, with the aid of an empirical table, small quantities of water in lard by observing the temperatures at which a melted lard remains clear.)

I shall consider here chiefly the sophistication of lard with vegetable oils (notably cotton seed oil and cotton seed stearine) and beef stearine. With regard to the latter it should be mentioned that the admixture of 5 per cent of beef stearine, as a "stiffener," was openly advocated by the trade as a necessary operation. Such admixture is now considered under the regulations of the "*Foods and Drugs Acts*" of the different countries as an adulteration. In order to "stiffen" soft lard, lard stearine (see p. 615) is now used. The employment of the latter did not come into vogue previously, as it requires four to five times as much lard stearine as it formerly took of beef stearine to obtain the desired consistence.

[1] *Arbeiten aus dem kaiserlichen Gesundheitsamte*, vol. xxv. 1907, Heft 2, p. 505. Cp. Fischer and Schellens, *Zeit. f. Unters. Nahrungs- u. Genussm.* 1908, xvi. 163.

In the chemical examination of a sample of lard very little importance should be attributed to the outward appearance, which was stated some years ago to offer a ready means of differentiating adulterated from genuine lard, the adulterated lard being supposed to exhibit a more or less polished surface, whereas genuine lard, whether crude or refined, was said to show a fine crystalline texture and a dull wrinkled surface. A differentiation of genuine lard from adulterated lard on the strength of the consistence may have been approximately possible at the time when American hogs were fed on wheat and the lard was hard; but since fattening with maize and also with cotton seed or cotton seed cake has been resorted to, the consistence has gradually become that of soft butter. It may be pointed out here that some Continental chemists endeavour to differentiate between American and home-rendered (leaf-) lards by the manner in which the melted lard solidifies ("*Wulstprobe*," *Langfurth* [1]).

The following physical and chemical methods are those employed in the detection of adulterants in lard :—

Specific Gravity.—The specific gravity should only be considered as a very rough corroboration of other tests, since some of the usual adulterants have nearly the same specific gravity as pure lard. However, as some analysts still attach value to this test it may be stated that cotton seed oil raises the specific gravity, as also does arachis oil. Therefore a sample having a higher specific gravity than 0·861 at 100° C. must be looked upon with suspicion.

The following table contains some specific gravities, reference to which will be found useful :—

Specific Gravity of Lard, Lard Adulterants, and Compound Lards

Kind of Fat.	Specific Gravity at °C.			Observer.
	37·8° (100° F.) (Water 37·8 = 1.)	99° (Water 15·5 = 1.)	100° (Water 40 = 1.)	
Pure lard . . .	0·905-0·907	0·860-0·861	0·85997-0·86191	Allen, Pattinson, Crampton
Lard stearine . .	..	..	0·8575-0·85792	Crampton
Cotton seed oil . .	..	0·868-0·8725	0·8672	Pattinson, Allen
,, . .	..	..	0·86681-0·86774	Leone and Longi
Cotton seed stearine	0·911-0·912	..	0·86463	Allen, Crampton
Beef stearine . .	..	0·8570	0·85444-0·85888	Pattinson, Crampton
Arachis oil . .	..	0·8673	..	Allen
Cocoa nut oil . .	0·910-0·916	0·8736	..	Moore
Compound lard No. 1	..	..	0·86121-0·86222	Crampton
,, No. 2	..	..	0·86289	,,

Fairley and *Cooke* [2] determined the specific gravities at 50° C. of the following mixtures of lard and cotton seed oil :—

[1] Cp. also Soltsien, *Pharm. Zeit.* 1894, 350. E. Seitter (*Zeit. f. Unters. Nahrungs- u. Genussm.* 1908, xv. 484) believes that home-rendered (German) lard can be differentiated from American lard by the occurrence of small quantities of soap in the former lard.

[2] *Journ. Soc. Chem. Ind.* 1890, 1162.

Mixtures of	I. Lard, 0·90038; Cotton Seed Oil, 0·90879.	II. Lard, 0·89159; Cotton Seed Oil, 0·89992.
Lard with 10 per cent of cotton seed oil .	0·90116	0·89246
,, 20 ,, ,, ,, .	0·90209	0·89328
,, 30 ,, ,, ,, .	0·90302	0·89421
,, 50 ,, ,, ,, .	0·90494	0·89617
,, 75 ,, ,, ,, .	0·90736	0·89850

Melting Point.—Although the melting point of a sample is not in itself of great importance (many adulterated lards having the same melting points as pure lard), still its determination should not be omitted. In the case of unadulterated hog's fat it is possible to ascertain from what part of the body the fat has been rendered; this will be seen by a glance at the following table :—

Melting Points of Lards from different parts of Hogs—North American and European

Source.	Fat from	Melting Point. °C.	Observer.[1]
American .	Foot (hoof)	35·1	Wiley
	Head	35·5	,,
	Leg	42·5	,,
	Ham	44·5	,,
European .	Back	33·8	Spaeth
	Kidney	43·2	,,
	Leaf	44	,,

In the last table, one number only is given for the melting point. It would seem that this melting point only refers to the final point when the lard in the capillary tube has become perfectly transparent. Since, however, lard in the process of melting first commences to soften, then passes through a stage of translucency till it has melted completely to a transparent liquid, and since this process extends over a range of several degrees, the interval should be stated, as is done in the following table :—

[1] Cp. also Dennstedt and Voigtländer's table, p. 574, and table, p. 575

Melting Points of Lards (Lewkowitsch)

		Iodine Value.
Lard from the leaf of an English hog[1] .	41·1-48·9	51·3
Lard from the shoulder ,, .	33·9-42·8	
Lard from the loin ,, .	33·9-42·2	
Lard from the back ,, .	27·2-33·9	
Irish bladder lard . . .	35·6-46·1	
English bladder lard . . .	33·9-45	
American lard	28·9-41·1	
American lard	33·0-42·0	
American lard	31·7-43·3	62·3
American lard	30·0-41·1	

Cp. also table, p. 565.

Goske,[2] taking the solidifying point of lard similarly as is done in the "Titer test," gives the following numbers:—

Fat.		Solidifying Point. °C.
Home-rendered lard	European .	27·10-28·62
,, ,,	,, .	26·64-29·34
,, ,,	,, .	29·10-29·95
Pure steam lard .	North American .	24·10-26·00
,, ,, .	,, .	25·05-25·5
,, ,, .	,, .	26·40-27·06
,, ,, .	,, .	24·9
,, ,, .	,, .	23·67-26·18
Adulterated lard .	. . .	30·50
,, ,, .	. . .	29·73-29·80
,, ,, .	. . .	29·90-30·15
,, ,, .	. . .	31·95-33·00
,, ,, .	. . .	35·90-36·58
,, ,, .	. . .	35·50-35·75

The adulterant in the last samples was tallow, the presence of which was masked by the addition of lard oil.

Iodine Value.—In the present state of lard manufacture it is not possible to lay down limits within which the iodine values of commercial samples may vary. As the lower limit of the iodine value of European leaf-lard, 46 was given in the second edition of this work. During the last few years, genuine lards rendered in the author's laboratory, from the leaf only, gave as high values as 53-60·44. Yet, the iodine value of the liquid fatty acids of the leaf-lard absorbing 60·44 per cent was 94·11 only. Nor can the upper limit of 63, given in the second edition of this work, be maintained, as during the last few years have been imported North American lards of grade (*d*) (p. 562), having iodine values exceeding even 70. A specimen of genuine North American lard examined in the author's

[1] English lard rendered by the author in the laboratory.

[2] *Journ. Soc. Chem. Ind.* 1893, 470.

laboratory absorbed 76·9 per cent of iodine (iodine value of liquid fatty acids 115·5). Still, a lard, the iodine value of which falls outside the range of 46 to 66, should be looked upon with suspicion, or in the case of lard above 66 as inferior lard (see table, p. 582). Of course, the converse does not follow, namely, that a sample with an iodine absorption within the limits named, must be pure, as combinations of fats of low (tallow, cocoa nut oil) and high iodine values (cotton seed, arachis, maize oils) enable the adulterator to prepare a variety of mixtures which will satisfy the limits named above. *Therefore a normal iodine absorption cannot be considered in itself as a final proof of purity.* Thus in the case of artificial lards made from steam lard, tallow stearine, and lard oil,[1] to the exclusion of vegetable oils, the iodine value will, as a rule, lie approximately within the above-named limits. The following table, due to *Goske*, gives the iodine values of several artificial lards calculated from those of its components, based on the following iodine numbers :—beef stearine, 20 ; steam lard, 65 ; mutton tallow, 40 ; lard oil, 85.

Fat.	Beef Stearine.	Steam Lard.	Mutton Tallow.	Lard Oil.	Calculated Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	10	90	...	...	60·5
2	15	85	...	...	58·25
3	...	70	30	...	57·50
4	25	45	...	30	59·75
5	35	25	40	...	57·27

The influence of exposure on the iodine value of lard may be gathered from the table, p. 576.

Provided adulteration with foreign fats be excluded, it is possible to ascertain with some measure of accuracy, by means of the iodine value, from what part of the animal the lard has been derived. This is shown in the following table :—

[1] In the United States edible lard oil is too valuable to be used for purposes of adulteration.

Source.	Fat from	Iodine Value.	Observer.
North American .	Head	85·03	Wiley
		66·2-70·4	v. Raumer
		65·0-66·6	Dennstedt and Voigtländer
		66·0-69·7	Mans
		63	Dupont
	Foot (hoof)	77·28	Wiley
		69·5-69·6	v. Raumer
		68·8	Dennstedt and Voigtländer
		69·4	Mans
		65	Dupont
	Back	63·6-66·7	v. Raumer
		64·7-66·3	Mans
		61·5-65·1	Dennstedt and Voigtländer
		61	Dupont
	Leaf	58	,,
		53·1	Spaeth
		52·55	Wiley
		60·4-66·7	v. Raumer
		59-63	Dennstedt and Voigtländer
		63·3-65·0	Mans
	Ham	67·7-69·0	v. Raumer
		66·6-68·4	Dennstedt and Voigtländer
		68·4-70·4	Mans
	Guts	60	Dupont
South American .	Head	59·7	Tortelli and Ruggeri
	Back	56·0	,, ,,
	Paunch	58·2	,, ,,
	Leaf	54·2	,, ,,
European—German .	Back	53·0-58·5	v. Raumer
		61·7	,,
	Leaf	50·4	,,
	Ham	55·0	Dennstedt and Voigtländer
Italian .	Head	59·2-68	Tortelli and Ruggeri
	Back	60·5-64·4	,, ,,
	Paunch	61-69·0	,, ,,
	Leaf	53·1-57·4	,, ,,

Steam lard, consisting as it does of the mixed fats from all, or from different parts of the animal, may therefore in some cases have a normal value, say up to 63, in other cases it may absorb more iodine, even as much as 76·9 (*Lewkowitsch*).

It will thus be obvious that the iodine value of the fat affords but limited information. Nor can the determination of the iodine value of the liquid fatty acids, which up to recently *did* furnish *reliable* indications of admixture of vegetable oils and fats, be considered as leading to a definite decision regarding the presence of adulterants. Whereas up to about ten years ago the rule held good that in the case of European lards the iodine value of the liquid fatty acids varied between 90 and 96, and in the case of American

lards between 95·2 and 106, these limits no longer apply; for, whilst *Bömer* found in a Westphalian lard, rendered by himself, the iodine value of the liquid fatty acids at 103·5, *Lewkowitsch* found in a North American lard as high a number as 115·5.

Even these high figures are exceeded by the iodine values of Chinese and Japanese lards from the back, and of their liquid fatty acids, as will be gathered from the table given on p. 590. Chinese lards have been imported already into Europe (Hamburg), and it appears also that lard from Cochin-China has been shipped to France.

In order to emphasise the importance which the iodine value has in the examination of lard, I have compiled the following tables :—

Fat or Oil.	Iodine Value of		Observer.
	Fat.	Liquid Fatty Acids.	
Lard, "Western Steam Lard"	65·4	104·5	Wallenstein and Finck [1]
,, American (18 samples)	58·4-62·9	95·2-104·9	Bömer [2]
	...	98-115·5	Lewkowitsch
,, Berlin	52·7	96·6	Wallenstein and Finck
,, Vienna	60·9	95·2	,,
,, Hungarian	60·4	96·2	,,
,, Roumanian	59·5	96·0	,,
,, Bavarian (5 samples)	52·2-61·2	92·8-96·6	v. Raumer [3]
,, Westphalian	52	93·5-103·7	Bömer
,, South American	...	92·8-100·6	Tortelli and Ruggeri
,, Italian	...	92-105·3	,,
Beef tallow, Australian	38·3	92·2	Wallenstein and Finck
,, Berlin	45·2	92·4	,,
,, Hungarian	38·6	92·7	,,
Cotton seed oil, American, white	108·0	147·5	,,
,, ,, ,, yellow	107·8	147·3	,,
,, ,, Egyptian, bleached	106·5	146·8	,,
,, ,, ,, yellow	108·0	148·2	,,
,, ,, Peruvian	106·8	147·8	Bömer
,, ,,	104·6-105·7	141·9-144·5	Wallenstein and Finck
Niger seed oil	133·5	147·5	,,
Maize oil	122·0	140·7	,,
Arachis oil	98·9	128·5	,,
Rape oil	101·1	120·7	,,
Olive oil	79·3-81·7	96·4-96·7	Bömer
Cocoa nut oil	8·0	54·0	Wallenstein and Finck

[1] *Journ. Soc. Chem. Ind.* 1894, 79.
[2] *Zeit. f. Unters. der Nahrungs- u. Genussm.* 1898, 539.
[3] *Zeit. f. angew. Chemie*, 1897, 210.

Source.	Fat from	Iodine Value of		Observer.
		Fat.	Liquid Fatty Acids.	
North American	Head I.	70·0-70·4	102·4	v. Raumer [1]
	,, II.	66·2-66·4	97·8-97·6	,,
	,, III.	68·2-68·4	101·2	,,
	Back I.	64·6-64·9	101·6-101·0	,,
	,, II.	63·6-63·6	102·8-102·3	,,
	,, III.	66·5-66·7	100·6-101·1	,,
	Leaf I.	66·4-66·7	103·0-102·6	,,
	,, II.	62·7-62·9	97·8-97·8	,,
	,, III.	60·4-60·7	96·9	,,
	Foot	69·5-69·6	98·6-98·3	,,
	Ham I.	67·9-67·9	101·6-101·0	,,
	,, II.	67·7-67·9	99·9-100·2	,,
	,, III.	68·7-69·0	103·0-103·2	,,
South American	Head	59·7	100·6	Tortelli and Ruggeri [2]
	Back	56·0	96·4	,, ,,
	Paunch	58·2	99·1	,, ,,
	Leaf	54·2	92·8	,, ,,
Italian . .	I. Head	68·0	98·2	Tortelli and Ruggeri
	Back	64·4	104·2	,, ,,
	Paunch	66·6	105·3	,, ,,
	Leaf	57·2	93·3	,, ,,
	II. Head	65·9	98·0	,, ,,
	Back	63·9	98·5	,, ,,
	Paunch	67·4	99·3	,, ,,
	III. Head	59·2	95·5	,, ,,
	Back	60·5	100·6	,, ,,
	Paunch	61·0	97·9	,, ,,
	Leaf	53·1	92·0	,, ,,
	IV. Head	65·6	103·3	,, ,,
	Back	61·9	102·3	,, ,,
	Paunch	69·0	104·9	,, ,,
	Leaf	57·4	94·0	,, ,,

Owing to the wide variations which the iodine values of the liquid fatty acids exhibit at present, they no longer afford the same certainty in judging a sample of lard as they did some years ago; we must even expect that the iodine values of genuine lards will slowly move in the direction of the upper limits. Whilst, then, the iodine value of the liquid fatty acids does not afford a definite means of detecting adulteration, still the determination of this value should not be omitted, since it furnishes cumulative evidence in the examination of those samples which must be regarded with suspicion. If the iodine value of the liquid fatty acids of a sample be found much above 110, a presumption is raised that adulteration with vegetable oils—such as cotton seed oil, maize oil—has taken place. On the other hand, if the iodine value of the liquid fatty acids lie much below 90, admixture with cocoa nut oil or palm kernel oil must be assumed.

[1] *Zeit. f. angew. Chemie*, 1897, 210. [2] *L'Orosi*, 1900, April.

It must, however, be repeated that if the iodine value of a sample under examination is found within the permissible limits, the lard cannot yet be pronounced unadulterated. For the admixture of a liquid vegetable oil may have been compensated by the addition of cocoa nut oil or, to some smaller extent, by beef tallow.

This test must, therefore, be supplemented in doubtful cases by special tests for cocoa nut oil and for tallow (see below).

Thermal Tests.—As a preliminary test, and in cases where a large number of samples must be examined quickly, the rise of temperature on mixing with concentrated sulphuric acid or with bromine may furnish useful results in a short time; this holds especially good of the second reagent.

Maumené Test.—The rise of temperature which occurs on mixing the sample with sulphuric acid has been recommended for the detection and even for the approximate estimation of cotton seed oil in lard by *Hehner*,[1] *Ambühl*, *Wiley*, and *Engler* and *Rupp*, whereas *Williams* failed to obtain decisive results. Since the modern methods of fat analysis have been introduced the examination by the *Maumené* test has become superfluous. In the opinion of the author too much value is ascribed to this test. However, as it is still being used, especially by French analysts, the following notes may be found helpful.

The numbers obtained by different experimenters vary so considerably, that the safest plan is to make comparative tests with pure specimens of lard and cotton seed oil before examining the sample. It need hardly be mentioned that the sample must be thoroughly dry before testing. The following table contains a few numbers obtained by various observers :—

[1] *Analyst*, 13 (1888), 166.

Fat.	Rise of Temp. °C.	Method Employed.	Observer.
Lard	24-27·5	50 grms. of fat; 10 c.c. conc. H_2SO_4	Hehner
Cotton seed oil	70	,, ,, ,,	,,
Lard	13-15	,, ,, ,, initial temp. 40° C.	Ambühl
Cotton seed oil	50-52	,, ,, ,, ,, ,, ,,	,,
"American" lard	30-35	,, ,, ,, ,, ,, ,,	,,
Lard	41·5	,, ,, ,, ,, ,, 35° C.	Wiley
Cotton seed oil	85·4	,, ,, ,, ,, ,, ,,	,,
Steam lard	38·8-42·1	,, ,, ,, ,, ,, ,,	,,
"Oleostearine"	20·8	,, ,, ,, ,, ,, ,,	,,
Lard stearine	37·7	,, ,, ,, ,, ,, ,,	,,
Artificial lards	42·1-58·9	,, ,, ,, ,, ,, ,,	,,
,, ,,	51·3-68·8	,, ,, ,, ,, ,, ,,	,,
Lard	31-32	,, ,, ,, ,, ,, not stated	Engler and Rupp
Cotton seed oil	81	,, ,, ,, ,, ,, ,,	,,
Lard with 10 per cent of cotton seed oil	34	,, ,, ,, ,, ,, ,,	,,
,, ,, 20 ,, ,, ,,	40-42	,, ,, ,, ,, ,, ,,	,,
,, ,, 50 ,, ,, ,,	58	,, ,, ,, ,, ,, ,,	,,
Lard	35	,, ,, ,,[1] ,, ,, 35° C.	Schweitzer and Lungwitz
Lard oil	45·3	,, ,, ,, ,, ,, ,,	,,
"Oleostearine"	31·9	,, ,, ,, ,, ,, 45° C.	,,
Cotton seed oil	61·5	,, ,, ,, ,, ,, 35° C.	,,
Compound lard	58·0	,, ,, ,, ,, ,, ,,	,,
Tallow	31·6	,, ,, ,, ,, ,, 45° C.	,,

[1] Acid of 100 per cent H_2SO_4, prepared by mixing fuming acid with conc. commercial acid.

In order to obtain more decisive results the liquid portion prepared by expression may be also examined (*Langfurth*).

Heat of Bromination.—The following numbers were obtained by *Hehner* and *Mitchell*;[1] the iodine values calculated from the temperatures observed are collated with those actually found with *Hübl's* solution :—

Fat.	I. Heat of Bromination. Rise of Temperature.	II. Iodine Value. Experiment.	III. Iodine Value calculated from I.
	°C.	Per cent.	Per cent.
Lard No. 1	10·6	57·15	58·3
,, 2	10·4	57·13	57·2
,, 3	11·2	63·11	61·6
,, 4	11·2	61·49	61·6
,, 5	11·8	54·69	64·9
,, 6	11·8	63·96	64·9
,, 7	10·2	57·15	56·1
,, 8	10·4	57·80	57·2
,, 9	9·0	50·38	49·5
,, 10	11·0	58·84	60·5
Lard + 10 per cent cotton seed oil	11·6	64·13	63·8

Refractometric Examination.—The refractometric examination should only be employed as a preliminary test. The numbers recorded in the following tables will then be found useful. It should be noted that the difference between European and American lards is not quite so distinctly shown in the refractometric indications as in the iodine absorption numbers.

Refractive Indices determined by means of the Butyro-refractometer

Kind of Fat.	European.		American.	
	Scale Divisions at 40° C.	Observer.	Scale Divisions at 40° C.	Observer.
Lard from head	...	...	52-52·6	Dennstedt and Voigtländer
,, ,, back	50·2-50·4	Mansfeld	51·8-52·4	,,
,, ,, leaf	51·2	,,	50·2-52	,,
,, ,, outer part of leaf	50·7	,,		
Lard from belly	50·4	,,		
,, ,, intestines	49·0	,,		
,, ,, foot	...	...	44·8	,,
,, ,, ham	...	...	51·9-53	,,
,, ,, ,,	49·1[2]	Bömer	49·7-51·8[3]	Bömer
Beef tallow	49·0	Mansfeld		
Horse fat	53·7	,,		
Cocoa nut oil	35·5	,,		
Cotton seed oil	61	,,		

[1] *Journ. Soc. Chem. Ind.* 1897, 88. [2] Liquid Fatty Acids, 42·8-42·2.
[3] Liquid Fatty Acids, 43·1-44·7.

Deviations in the Oleo-refractometer (Amagat and Jean)

Kind of Fat or Oil.	"Degrees" in the Oleo-refractometer.	
	Fat.	Fatty Acids.
Lard	−12·5	−30
Steam lard	−13	−30
Lard stearine	−10 to −11	
Beef tallow	−16; −17	−40
,, stearine	−34	
Veal tallow	−19	
Cotton seed oil	+20	+10
,, stearine	+25	+20
Sesamé oil	...	−18
Arachis oil	+5	
Lard with 10 per cent of beef tallow	−12	
,, ,, 20 ,, ,, ,,	−13	
,, ,, 50 ,, ,, ,,	−14	−33
,, ,, 5 ,, cotton seed oil	−10	
,, ,, 10 ,, ,, ,,	− 8	
,, ,, 15 ,, ,, ,,	− 7	
,, ,, 20 ,, ,, ,,	− 6	
,, ,, 25 ,, ,, ,,	− 5	
,, ,, 30 ,, ,, ,,	− 4	
,, ,, 40 ,, ,, ,,	0	
,, ,, 50 ,, ,, ,,	− 3	
,, ,, 5 ,, ,, stearine	−11	
,, ,, 10 ,, ,, ,,	− 7	
,, ,, 20 ,, ,, ,,	− 4	
,, ,, 30 ,, ,, ,,	− 3	
,, ,, 40 ,, ,, ,,	− 2	
,, ,, 50 ,, ,, ,,	+ 1	
Lard with 20 per cent of arachis oil	− 8	−23
,, ,, 20 ,, sesamé ,,	...	−20
,, 40 per cent; beef tallow 40 per cent; cotton seed oil 20 per cent	...	−24
Steam lard 60 per cent; beef tallow 15 per cent; arachis oil 25 per cent	− 8	
Lard 60 per cent; mutton tallow 25 per cent; arachis oil 15 per cent	−13	−22
Cocoa nut oil	−54	

From the following table, due to *Dupont*,[1] it will be seen that American lards show smaller deviations than European lards; if judged solely by the standard of European lards, they might be rashly condemned as containing cotton seed oil:—

[1] *Journ. Soc. Chem. Ind.* 1895, 828.

[TABLE

American Lard.	Oleo-refractometer. Deviation.	Iodine Value.
From leaf . .	−11·5	58
,, back . .	−5	61
,, intestines .	−7	62
,, head . .	−7	63
,, foot . .	−4	65
Gut lard . .	−11	60
Rancid lard . .	−7	63
,, lard . .	−6·5	64

The influence of rancidity on the refractometric index is illustrated by the numbers given in the following table; they are contrasted with the *Reichert-Meissl* values (*Spaeth*):—

"Degrees" in the Butyro-refractometer calculated for 25° C.		Reichert-Meissl Values.
After 1 year.	After 3 years.	After 3 years.
59·35	62·60	...
60·21	62·30	4·3
60·49	62·45	9·36
57·71	58·75	1·32
60·35	62·70	...
61·35	63·10	...
58·14	63·1	3·74

The refractive indices rise in the same proportion as do the iodine values. This is, of course, due to the influence of the unsaturated fatty acids (the amount of which is indicated by the iodine value) on the refractive index. This will be gathered from the following table:—

[TABLE

Lard.	Butyro-refractometer. "Degrees" at 40° C.	Iodine Value		Solidifying Point. °C.	Melting Point. °C.	Observer.
		Of Fat.	Of Liquid Fatty Acids.			
Chinese Lard . .	50·0-53·7	58·1-82·0 [1]				Farnsteiner [2]
Chinese fat from back	53·3-54·4	79-80·8	113·3-121·7			,,
Japanese fat from back	53·8-57·3	80·0-101·7	124·2-138·7			,,
Japanese fat from ham	51·4-55·9	71·5-98·6	111·1-131·5			,,
English lard from :—						
Leaf . . .	48·4	55·9		30·5-32·7		Dunlop
Leaf . . .	48·1	53·0		30·5-31·5	47	,,
Kidney bed . .	48·3	55·3		33·3-33·7		,,
Kidney bed . .	48·2	53·4		33·7-35·0	50	,,
Kidney bed . .	49·2	58·1		27·0-27·8	43	,,
Leg . . .	48·6	57·5		29·0-30·0		,,
Leg . . .	50·0	64·1		24·3-25·5	37	,,
Leg . . .	50·0	65·4		27·6-27·9		,,
Head (cheek) . .	49·4	62·9		26·0-26·7		,,
Back . . .	49·0	58·4		28·0-28·3		,,
Back . . .	49·7	64·2		26·7-26·8	38	,,
Back . . .	50·7	67·9		25·3	36	,,

The determination and investigation of the **unsaponifiable matter** is of importance in the examination of a suspected lard.

In the early years of lard manufacture on a large scale, adulteration with paraffin wax, up to 20 per cent, had been practised in the United States ; but this mode of adulteration was soon abandoned. During the last few years American lards have been imported containing about 2 per cent of unsaponifiable matter, consisting chiefly of paraffin wax.[3] This may have been introduced into lards adulterated with vegetable fats, in order to defeat the indications furnished by the phytosteryl acetate test. But if this be the only reason, the adulteration would be a very clumsy one, for the added paraffin wax would amount to over 1·5 per cent of the lard, a quantity that can be readily recognised by the appearance of the acetylated unsaponifiable matter when crystallising it from alcohol. (As to another likely reason for the large amount of added paraffin wax, see below, "*Wesson's* test.") *Polenske*[4] has shown that quantities falling below 0·1 per cent of paraffin wax (reckoned on lard) are sufficient so to depress the melting point of the acetates in the phytosteryl acetate test that the presence of vegetable fats in a lard would no longer be recognised. In order to show how far the addition of paraffin wax may defeat the indications of the phytosteryl acetate test, *Polenske* experimented with 0·1 gram of a mixture consisting of 94 per cent of cholesterol and 6 per cent of phytosterol, to which varying amounts of paraffin wax were added. The quantity of 0·1 gram was chosen because 100 grams of lard yield about 0·1 gram of pure cholesterol. This mixture of cholesterol and

[1] In four specimens, 82·1-85.

[2] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1905, x. 70.

[3] Olig and Tilmans, *Zeit. f. Unters. Nahrungs- u. Genussm.* 1905, ix. 597.

[4] *Arbeiten. a. d. kaiserl. Gesundheitsamte*, 1905, xxii. 576.

phytosterol gave in the phytosteryl acetate test the following numbers :—

Melting point of the 3rd crop of crystals . .	118° C.
,, ,, ,, 4th ,, ,, . .	119° C.
,, ,, ,, 5th ,, ,, . .	120° C.

The following table reproduces the results obtained with mixtures containing paraffin wax :—

Melting Points of Acetates obtained from 0·1 *Gram of a Mixture of* 94 *per cent of Cholesterol and* 6 *per cent of Phytosterol, to which varying amounts of Paraffin Wax have been added.*

	Grams of Paraffin Wax added.							
	0·002	0·003	0·005	0·007	0·01	0·02	0·05	0·1
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Melting points of the 3rd crop of crystals.	117·5	117·5	116·5	115	113	104	79	64
Melting points of the 4th crop of crystals.	118·5	118	117	112	108	89	60	55
Melting points of the 5th crop of crystals.	120	119·5	118	115	112	...	55	53

The amounts of paraffin wax added to the mixture of cholesterol and phytosterol are, therefore, in the order of the vertical columns—2 per cent, 3 per cent, 5 per cent, 7 per cent, 10 per cent, 20 per cent, 50 per cent, 100 per cent; or, calculated on lard, 0·002 per cent, 0·003 per cent, 0·005 per cent, 0·007 per cent, 0·010 per cent, 0·02 per cent, 0·05 per cent, 0·1 per cent. It will thus be seen that as little as 0·007 to 0·01 per cent of paraffin wax in lard is capable of nullifying the indications of the phytosteryl acetate test, smaller quantities are practically without any influence, whilst larger quantities are readily detected.

Polenske has indicated a process for removing the paraffin wax, and, furthermore, a method for ascertaining its quantity. I have repeated *Polenske's* experiments, and can fully confirm their correctness.

In order to ascertain the influence of paraffin wax on pure cholesteryl acetate, I prepared mixtures of pure cholesteryl acetate, of the melting point 113°-113·5° C., and of paraffin wax, and determined their melting points.

Melting Point of Mixtures of Cholesteryl Acetate, Melting Point 113·5° *C., with Paraffin Wax (Lewkowitsch)*

	Melting Point.
97 per cent cholesteryl acetate + 3 per cent paraffin wax .	. 110° C.
93 ,, ,, ,, +7 ,, ,, ,, .	. 106° C.

When a mixture of 90 per cent of cholesterol and 10 per cent of paraffin wax is acetylated, the presence of the latter can be detected at once by the appearance of a droplet of paraffin wax floating on the acetic anhydride solution. On subjecting the acetylated mass to recrystallisation, as is done in the phytosteryl acetate test, the following results were obtained :—

Melting point of the	2nd	crystallisation	.	.	.	90°-99° C.
,,	,,	,,	3rd	,,	.	.	.	90°-98° C.
,,	,,	,,	4th	,,	.	.	.	86°-89° C.
,,	,,	,,	5th	,,	.	.	.	86°-92° C.

It will thus be seen that the melting point falls rapidly, as must indeed be expected, since the paraffin wax, being insoluble in alcohol, separates in its entirety, together with a gradually diminishing amount of cholesteryl acetate.

As a corollary to these data, the result of experiments with 3 per cent of paraffin wax are given in the following table [1] :—

Acetates from a Mixture of 97 *per cent of Cholesterol and* 3 *per cent of Paraffin Wax* (*Lewkowitsch*)

Melting point of the	1st	crop of crystals	.	.	.	104°-108° C.
,,	,,	,,	2nd	,,	,,	.	.	.	104°-109° C.
,,	,,	,,	3rd	,,	,,	.	.	.	103°-109° C.
,,	,,	,,	4th	,,	,,	.	.	.	103°-109° C.
,,	,,	,,	5th	,,	,,	.	.	.	103°-108° C.

The removal of the paraffin wax from the crude unsaponifiable matter is carried out, according to *Polenske's* directions, by treating the unsaponifiable matter obtained from 100 grams of fat with 1 c.c. of petroleum ether (boiling below 50° C.) for twenty minutes in a water-bath at 15°-16° C., transferring the mass to a small funnel closed with cotton wool, and washing with five successive portions each of one-half c.c. of petroleum ether. The paraffin wax is thus readily removed, whereas cholesterol and phytosterol, being much less soluble in cold petroleum ether, remain on the filter. The residue on the filter is then acetylated, and further treated as is usual in the phytosteryl acetate test. The drawback of this method is that a certain amount of the alcohols is washed away, but it offers the countervailing advantage that more cholesterol is removed than phytosterol, so that the indications of the phytosteryl acetate test become more distinct, the proportion of phytosterol (if any) to cholesterol being increased.

Polenske's method for the quantitative determination of paraffin wax consists in treating the unsaponifiable matter from 100 grams of fat with 5 c.c. of concentrated sulphuric acid in a glycerin bath at 104° to 105° C. for one hour, when the alcohols are destroyed and the paraffin wax remains behind. The latter is extracted with low

[1] Lewkowitsch, *Chem. Rev.* 1907, No. 3.

boiling petroleum ether, and weighed. In case minute quantities only of paraffin wax be present, the treatment with sulphuric acid should be repeated.

The following table, due to *Polenske*, shows the accuracy of the determination of paraffin wax in mixtures prepared from cholesterol and paraffin wax :—

	0·1 gr. of Cholesterol, to which had been added Paraffin Wax.					
	0·003 gr.	0·004 gr.	0·005 gr.	0·01 gr.	0·1 gr.	0 gr.
	Yielded Paraffin Wax.					
	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
1. After 1st treatment with sulphuric acid .	0·0041	0·0056	0·0063	0·014	0·096	0·0029
2. After 2nd treatment with sulphuric acid .	0·0033	0·0041	0·0055	0·0105	0·092	0·0005

Unfortunately, by employing this method, the alcohols are destroyed, so that a confirmatory test cannot be carried out. From a somewhat extended experience of this test the author[1] has been led to adopt the following method :—The unsaponifiable matter of the suspected fat is converted into acetate in the usual manner. By observing the appearance of the acetic anhydride solution, paraffin wax amounting to 10 per cent of the alcohols can be detected at once by the appearance of a globule on the acetic anhydride solution. This can be filtered off and, after washing with absolute alcohol, weighed. When determining the melting points of the consecutive crops of acetates the above-given tables will serve as guides. Only in case the presence of about 0·005 to 0·01 per cent of paraffin wax be suspected, further examination is required. In that event all the crystals and the mother liquors from the several crystallisations are united and boiled down to dryness. The mixture of acetates and of paraffin wax (if any) is saponified with alcoholic potash, and the soap solution extracted with ether, so as to recover the original unsaponifiable matter. If the work has been carried out with due care, the saponification value of the dried mass should be determined, as important information may thus be gained. This is brought out by the experiments detailed in the following table :—

[1] Lewkowitsch, *Chem. Rev.* 1907, No. 3.

[TABLE

Saponification Values of Mixtures of Cholesteryl Acetate and Paraffin Wax (Lewkowitsch)

	Calculated.	Found.
Cholesteryl acetate . . .	135·5	...
I. 0·1146 grm. cholesteryl acetate +0·0100 grm. paraffin wax .	124·6	121·5
II. 0·1138 grm. cholesteryl acetate +0·0200 grm. paraffin wax .	115·2	117·3

The paraffin wax can then be determined quantitatively in the recovered unsaponifiable matter as directed above.

Whereas adulteration with vegetable oils and fats can be detected with certainty by the phytosteryl acetate test, the recognition of beef tallow and beef stearine ("oleostearine") presents considerable difficulties, the more so as small quantities, down to 5 per cent, may repay the cost entailed in the mixing.

In the following lines special methods for the detection of the more important adulterants are indicated.

Vegetable Oils

The phospho-molybdic acid test (Vol. I. Chap. VII.) has been recommended by several observers as a method to indicate with certainty the presence of vegetable oils in lard. The author has, however, shown [1] that a slightly rancid lard also reduces the reagent, and, furthermore, that an admixture of less than 15 per cent of cotton seed oil with pure lard cannot be thus detected. This test can therefore only be admitted as a preliminary one. The author's experiments have been repeated and confirmed by other observers (*Samelson* and *Tennille*).

The surest proof of the presence of vegetable oils is obtained by the phytosteryl acetate test. Even 1-2 per cent of vegetable oils may thus be detected. Since this test is somewhat cumbersome and lengthy in the practice of an analytical chemist, and will therefore only be resorted to when other methods fail to give a decisive answer, the determination of the iodine value of the sample and of its liquid fatty acids should be looked upon as the readiest means of furnishing preliminary information.

If the probable presence of a vegetable oil has been indicated by

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1894, 619.

an abnormally high iodine value, one of the following four oils should be specially looked for:—Arachis oil, sesamé oil, cotton seed oil (cotton seed stearine), maize oil.

Arachis Oil.—*Renard's* test should give a positive result; the amount of arachis oil present can be approximately calculated from the weight of the crude arachidic acid obtained. It should be emphasised that it is necessary to determine the melting point of the "arachidic acid"; if it be found to be below 70° C., the precipitate must be recrystallised.[1]

Sesamé Oil.—This would be readily detected by *Baudouin's* reaction. It should, however, be noted that quite recently *König* and *Schluckebier*[2] demonstrated that on feeding pigs with sesamé cake the substance which gives the *Baudouin* reaction passes into the body-fat. This was proved by examining the fat taken from five different parts of the animal (head, back, leaf, ham, intestines) which had served for the experiment.

Cotton Seed Oil (Stearine).—For the preliminary detection of cotton seed oil or cotton seed stearine in lard the colour reactions described p. 162 may be employed. The most useful amongst these is the *Halphen* test. It has been stated already that an over-estimation of the indications furnished by this test may lead to grave errors. If a positive *Halphen* colour reaction has been obtained, the presumption is raised that the sample of lard is adulterated with cotton seed oil. It must, however, be distinctly understood that no more than a presumption is raised, for a positive test does not indicate with certainty that cotton seed oil is present, nor does a negative test prove its absence. For, as pointed out already, the colouring matter contained in cotton seed passes into the lard from hogs fed on cotton cake. This has been placed beyond doubt by several observers (*Langfurth*,[3] *Soltsien*,[4] *Fulmer*[5]). Hence it would be entirely misleading to conclude from a positive *Halphen* reaction that cotton seed oil is present. More erroneous still would it be to judge from the depth of the tint as to the approximate amount of cotton seed oil present. I lay stress on this, as attempts have been made to convert the *Halphen* test into a colourimetric quantitative reaction. *Langfurth* has shown that lard obtained from a hog fed experimentally on cotton cake gave as strong a colouration as was obtained by a mixture of lard with 30 per cent of cotton seed oil; he therefore rightly points out that the quantity of lard obtained from a single hog fed on cotton cake would be quite sufficient to contaminate a tank-car of lard, so that the mixture would give a very distinct colouration in the *Halphen* test.

Fulmer has more recently carried out systematic experiments by feeding pigs with cotton seed meal and testing the fat obtained from different parts of the body of the animal. The chromogenetic sub-

[1] Cp. W. B. Smith, *Journ. Amer. Chem. Soc.* 1907, 1756.
[2] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1908, xv. 648.
[3] *Zeit. f. angew. Chem.* 1901, 685. [4] *Zeit. f. öffentl. Chem.* 1901, 140.
[5] *Journ. Amer. Chem. Soc.* 1902, 1148; 1904, 837.

stance in cotton seed oil passes into all parts of the body, but the intensity of the *Halphen* test was found greater in the fat from the leaf and back than in that from the head. Judged solely by the *Halphen* test, the conclusion might have been derived that some of the lards contained up to 15 per cent of cotton seed oil.

Dunlop[1] confirmed this by examining lards from a pig which had been fed for six weeks with decorticated cotton seed meal (from 1 to 1·5 lb. per day). The numbers in the last column of the following table give the percentages of cotton seed oil that might have been judged to be contained in the lards, if the *Halphen* test alone were taken as the guide.

Lard from a Pig fed on Cotton Seed Meal

Part of Animal.	Iodine Value.	Butyro-refracto-meter at 40° C. "Degrees."	Cotton Seed Oil, by Halphen's colour test. Per cent.
Shoulder . . .	67·8	50·7	10
Leg	65·1	50·3	8
Back	64·8	50·0	10
Leaf	58·3	49·0	2
Kidney bed . .	58·3	49·0	6

If, therefore, on examining a specimen of lard a colouration has been obtained, further tests must be applied, especially the phytosteryl acetate test. Indeed, *Tolman*[2] has shown that the lards obtained by *Fulmer* from pigs fed on cotton seed meal gave normal numbers in the phytosteryl acetate test. In the absence of vegetable fats a positive *Halphen* test would therefore indicate that feeding with cotton seed or cotton seed meal had taken place. If employed with due precaution, the *Halphen* test will be found a very useful preliminary test, especially in those cases where a large number of samples must be examined rapidly. A negative *Halphen* test, as has been pointed out already, does not prove the absence of cotton seed oil, since cotton seed oils which have been heated do not give a colouration with *Halphen's* reagent.

If the *Halphen* reaction give a negative result, the **nitric acid** test may be usefully applied as a further preliminary one, for, as shown above (p. 164), cotton seed oil after heating still gives a brown colouration. But it must be remembered that lards from hogs fed on cotton cake also give a brown colour. Still, the absence of a brown colouration may indicate the absence of any considerable quantities of cotton seed oil.

The reduction of silver nitrate (by any of the methods described p. 164) by no means proves the presence of cotton seed oil. Lard obtained from hogs fed on cotton cake reduces the *Becchi* reagent

[1] *Journ. Soc. Chem. Ind.* 1906, 458. [2] *Journ. Amer. Chem. Soc.* 1905, 589.

strongly. Even lards obtained from normally fed hogs occasionally reduce silver nitrate solution (*Wesson*,[1] *Mariani*, *Bevan*[2]).

To illustrate the foregoing remarks by an example, I give a short summary of an examination (carried out in my laboratory) of a specimen of lard which gave the following indications :—

Iodine value of lard	76·5
Iodine value of the liquid fatty acids . .	115·5
Unsaponifiable matter	0·35 per cent.

Halphen test ; a slight colouration was observed, such as would be indicated by a lard containing an admixture of about 6 per cent of cotton seed oil.

The high iodine value in conjunction with the positive *Halphen* test raised the presumption that this lard was adulterated with cotton seed oil. Hence the examination by the phytosteryl acetate test became imperative.

A preliminary microscopic examination of the unsaponifiable matter (cp. Vol. I. Chap. IX. (*a*)) showed that phytosterol was absent, the characteristic crystals of cholesterol only having been observed. The unsaponifiable matter was then examined by the method described (Vol. I. Chap. IX.) with the following result :—

Crystals.	Melting Point. °C.
2nd crop	113
3rd crop	114-114·5
4th crop	115
5th crop	113-114

From these results it became evident that the lard was free from cotton seed oil or any other vegetable oil.

As lard gives a liquid product with **sulphur chloride**, which is soluble in carbon bisulphide, cotton seed oil may also be detected qualitatively by means of that reagent (*B. Warren*, *Jones*[3]). In the presence of cotton seed oil a hard mass partly insoluble in carbon bisulphide is produced.

The author has tried this method and found it useful as a preliminary test. His observations are given in the following table :—

[1] *Journ. Chem. Soc.* 1894, Abstr. II. 75. [2] *Analyst*, 1894, 88.
[3] *Ibid.* 1888, 170.

[TABLE

Mixtures of Lard and Cotton Seed Oil (Lewkowitsch)

5 grms. of fat dissolved in 2 c.c. CS_2, added 2 c.c. S_2Cl_2, and placed on the water-bath

Lard. Per cent.	Cotton Seed Oil. Per cent.		Solubility of Product in Carbon Bisulphide.
100	0	No reaction	Completely soluble
90	10	Thickens after 35 minutes	,, ,,
80	20	,, ,, 30 ,,	52 per cent ,,
70	30	,, ,, 26 ,,	39·6 ,, ,,
60	40	,, ,, 18 ,,	34·8 ,, ,,
50	50	Solid after 10 ,,	37·4 ,, ,,
40	60	,, ,, 8 ,,	30·6 ,, ,,
30	70	,, ,, 7 ,,	32·6 ,, ,,
20	80	,, ,, 6 ,,	30·0 ,, ,,
10	90	,, ,, 4 ,,	28·4 ,, ,,
0	100	,, ,, 3 ,,	24 ,, ,,

It is advisable to test the sample side by side with pure lard, or better still, with mixtures of lard and cotton seed oil (or cotton seed stearine) prepared in a similar fashion to that illustrated by the table.

Maize Oil.—If arachis and sesamé oils are absent, an abnormally high iodine value can only be due to cotton seed oil or maize oil (with regard to Chinese lard, see above). The solidifying point of the mixed fatty acids would in this case lead to a decision if only one oil be present. If both are present, this method breaks down.[1]

If the iodine value of the lard or of the mixed fatty acids is abnormally low, then the presence of cocoa nut oil or palm kernel oil may be suspected.

Cocoa nut oil or **palm kernel oil** will be recognised by a high saponification value, and especially by a definite *Reichert* value and a notable amount of insoluble volatile acids of the sample.

In order to render the indications of this test still more decisive, the suggestion made by *Mecke*[2] may be adopted, viz. to treat one part of the sample with two parts of 95 per cent alcohol at about 60° C. with frequent shaking. Cocoa nut oil passes into the alcohol to a much greater extent than lard does. After distilling off the alcohol from the alcoholic solution the residual fat is examined, when its saponification value, *Reichert* value, titration number of the insoluble volatile acids (see "Butter Fat"), and also the iodine value will afford important information. *Morrschöck*[3] has shown that in case

[1] Cp. M'Pherson and W. A. Ruth, *Journ. Amer. Chem. Soc.* 1907, 921.

[2] *Zeit. f. öffentl. Chemie*, 1904, 9.

[3] *Zeit. f. Unters. d. Nahrungs- u. Genussm.* 1904, vii. 586.

pure lard is tested as described here, the extracted fat is characterised by a considerably higher iodine absorption than that of the original lard.

Experiments carried out by *Arnold*[1] according to the method described p. 572, and detailed in the following table, show the manner in which this procedure may be applied for quantitative purposes :—

[1] *Zeit. f. Unters. d. Nahrungs- u. Genussm.* 1907, xiv. 179.

[TABLE

	Butyro-refracto-meter at 40° C. "Degrees."	Saponification Value.	Reichert-Meissl Value.	Molecular Weight of the Soluble Volatile Acids.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids (Polenske's Method, 5 grms.).	Molecular Weight of the Insoluble Volatile Acids.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids for 0·5 grms. of Fat (Polenske's Apparatus).	Molecular Weight of the Insoluble Volatile Acids.	Iodine Value.	Non-Volatile Fatty Acids.			150 grms. yielded Alcohol-soluble Portion. Grms.
										Butyro-refracto-meter at 40° C. "Degrees."	Neutralisation Value.	Iodine Value.	
American Lard mixed with 10 per cent of Cocoa Nut Oil													
I. Original Fat . .	49·8	195·4	0·55	...	0·60	...	0·55	...	62·0	36·4	204·4	62·9	...
II. Alcohol-soluble Fat .	51·0	194·3	2·50	136·1	1·25	...	0·85	...	64·4	39·7	203·3	66·5	12
III. Alcohol-insoluble Fat	49·8	196·0	0·55	...	0·55	...	0·50	...	60·4	36·1	204·9	62·7	...
American Lard mixed with 3 per cent of Cocoa Nut Oil													
I. Original Fat . .	49·6	196·0	1·00	...	0·70	...	...	...	61·1	35·3	203·8	62·1	...
II. Alcohol-soluble Fat .	49·3	205·5	4·13	139·2	2·35	...	...	...	60·5	37·0	211·1	64·1	9
III. Alcohol-insoluble Fat	50·0	197·7	0·90	...	0·75	...	...	...	59·9	36·6	205·9	61·3	...
German Lard mixed with 4 per cent of Cocoa Nut Oil													
I. Original Fat . .	48·9	202·7	1·50	...	0·80	...	...	...	47·1	34·9	210·8	48·6	...
II. Alcohol-soluble Fat .	49·1	216·2	5·70	136·7	3·50	194·2	1·70	208·3	45·7	36·2	222·5	49·6	9·9
III. Alcohol-insoluble Fat	49·0	201·6	1·10	...	0·70	...	...	...	46·3	34·2	209·5	49·5	...
German Lard mixed with 4 per cent of Cocoa Nut Oil													
I. Original Fat . .	49·1	201·1	1·80	...	0·85	...	0·65	...	61·7	...	...	...	...
II. Alcohol-soluble Fat .	48·7	210·0	5·56	132·0	3·25	191·0	1·55	...	55·3	...	...	...	9·1
American Lard mixed with 5 per cent of Cocoa Nut Oil													
I. Original Fat . .	49·2	198·8	1·35	...	0·90	...	...	...	60·0	35·0	206·7	62·0	...
II. Alcohol-soluble Fat .	49·0	210·6	5·60	142·0	3·95	190·0	...	...	52·7	36·1	216·4	58·3	9·1
III. Alcohol-insoluble Fat	50·0	197·1	1·00	...	0·75	...	..	...	58·8	...	...	...	...
American Lard mixed with 10 per cent of Cocoa Nut Oil													
I. Original Fat . .	48·3	202·2	2·37	...	1·30	...	...	...	55·4	33·8	209·2	56·2	...
II. Alcohol-soluble Fat .	46·9	229·0	8·00	135·3	7·85	178·0	...	...	39·7	32·0	231·9	42·8	10·2
III. Alcohol-insoluble Fat	49·2	200·0	1·90	...	1·10	...	...	...	55·5	34·0	207·5	56·9	...

In doubtful cases the phytosteryl acetate test—provided other vegetable oils be absent—will furnish conclusive evidence.[1]

Animal Fats

The detection of **tallow** and (or) **beef stearine** in lard is a difficult problem, and can only be solved successfully, in the present state of our knowledge, by strict comparison with samples of pure lards from different parts of the body of hogs, and of the same lards mixed with known proportions of the suspected adulterant. This problem is rendered all the more difficult as lards of different origin vary greatly in their composition, as is shown in the above-given tables.

The first attempts to detect small quantities of beef fat or beef "stearine" in lard were made in the year 1883 by *Belfield* and by *Delafontaine*, both basing themselves on the method published by *Husson*[2] in 1878.

Belfield claimed to be able to detect 10 per cent of beef stearine in lard. He directed to dissolve the sample in ether, and examine under the microscope the crystals which separate from the ethereal solution. Forty drops of the melted lard are dissolved in 10 c.c. of ether in a test-tube and allowed to cool (*Pattinson*[3]). Should no crystals form, the cork is removed from the tube and a loose plug of cotton-wool substituted, when crystals will be obtained by the spontaneous evaporation of the ether. If the crystals have been formed too rapidly it is best to redissolve them by addition of more ether. Some of the crystals are then placed on an object-glass and examined microscopically. Crystals from pure lard usually form oblong plates — either singly or in bunches — and have oblique terminals, whereas those from beef tallow form curved tufts of very thin needles somewhat of the shape of an "*f*" ("plumose" crystals). Cp. Figs. 8, 9, 10.

The author examined microscopically the crystals obtained from specimens of leaf lard, lard from the loin, lard from the shoulder, and lard from the back, all of which were rendered in his laboratory. Forty drops of the melted fat were dissolved in 10 c.c. of ether, and were allowed to crystallise under exactly the same conditions in corked test-tubes.

In the case of *leaf* lard, bunches of crystals were obtained, which under a low power of magnification appeared as needles, but under a higher power were distinctly discernible as plates.

The lard *from the shoulder* yielded some isolated plates, but mostly bunches, radiating from a centre point in all directions, thus forming a whole circle or parts thereof. There also appeared bunches of crystals which were very similar to tallow crystals; yet under a high power of magnification they showed the chisel-shaped ends characteristic of lard crystals. Small bunches of crystals were, however,

[1] With regard to Robin's method, cp. *Annal. Chim. Analyt. Appl.* 1907, **12**, 87. Hoton's acetic acid test is referred to in Vol. I. Chap. V.

[2] *Journ. Pharm. Chim.* (4) 27, 100. [3] *Journ. Soc. Chem. Ind.* 1889, 30.

noticed which were indistinguishable from beef tallow crystals. Moreover, in various preparations the plates did not even predominate over those crystals which appeared to be most like beef crystals.

The lard *from the loin* showed many distinct straight plates with the chisel-shaped ends characteristic of lard crystals. These were even noticeable in the thickest plates which at first, under a low power, appeared like beef crystals. A number of plates were observed, especially amongst those in the bunches, which were curved, and as they had the shape of distinct plates, would appear to represent the transition form of plates to needles.

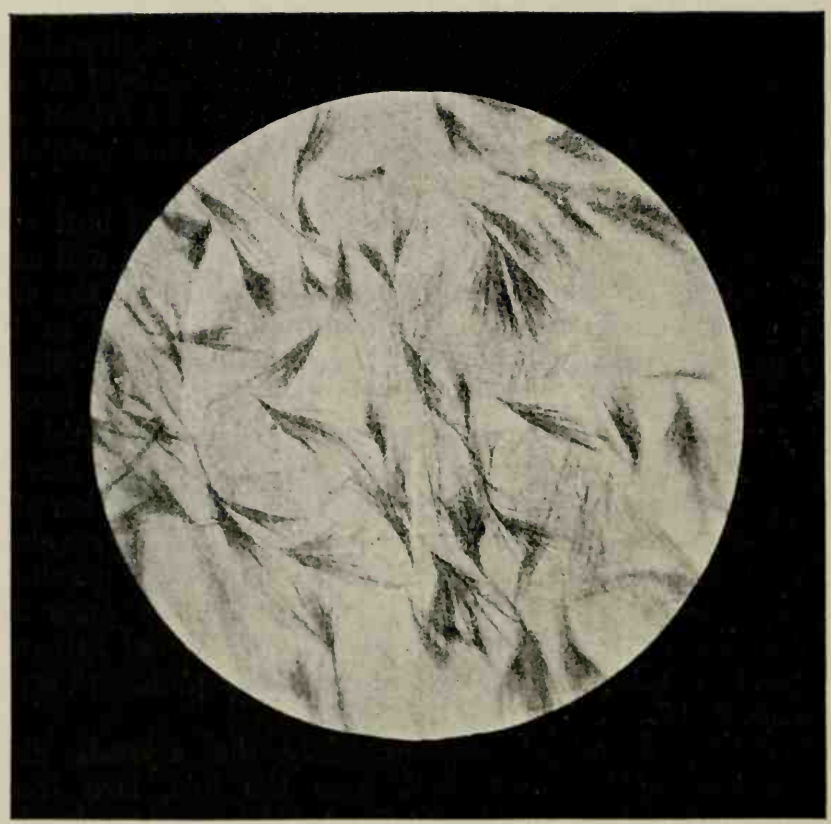

Fig. 8.—Mutton Tallow Crystals. 50 diam.

The lard *from the back*, which took the longest time to crystallise (no doubt because it was the softest lard), showed distinct plates throughout, both as regards the isolated crystals, as also those heaped in bunches. The plates were much longer than those obtained from any other part. This is most likely due to the time required for crystallisation having been so much longer.

Mixtures of lard from the back-fat with 5 to 10 per cent of tallow, prepared by the author, showed distinct plates of lard crystals side by side with distinct bunches, which, even under a magnification of 670, could not be recognised as having chisel-shaped ends; these were possibly plates lying on their ends, thus appearing as needles. Still, it would be hazardous to pronounce a definite opinion on the strength of these microscopic indications.

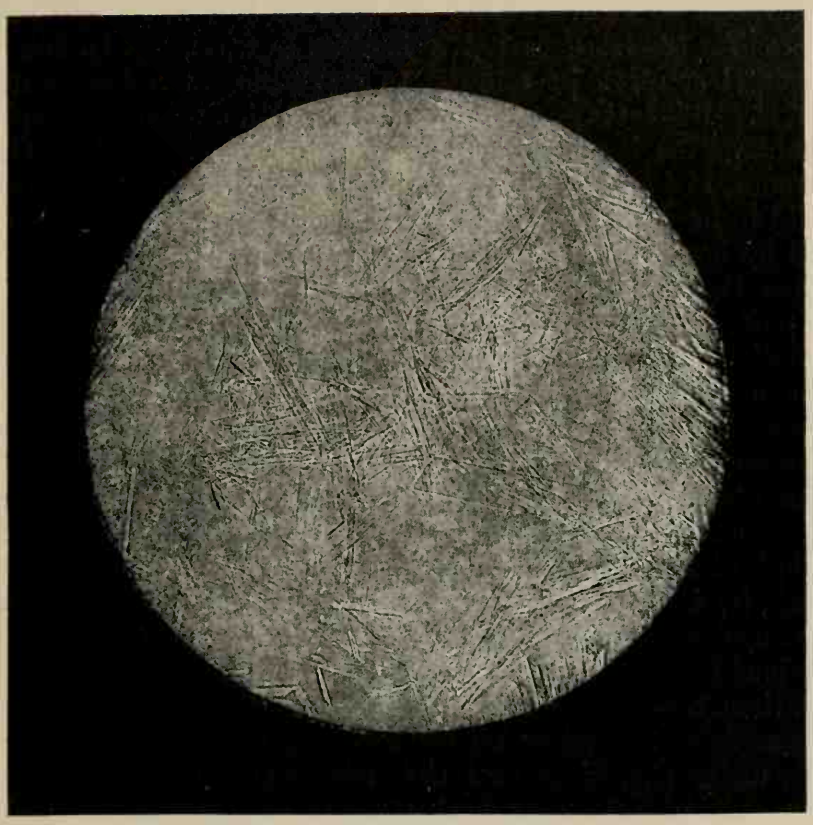

Fig. 9.—Lard Crystals. 50 diam.

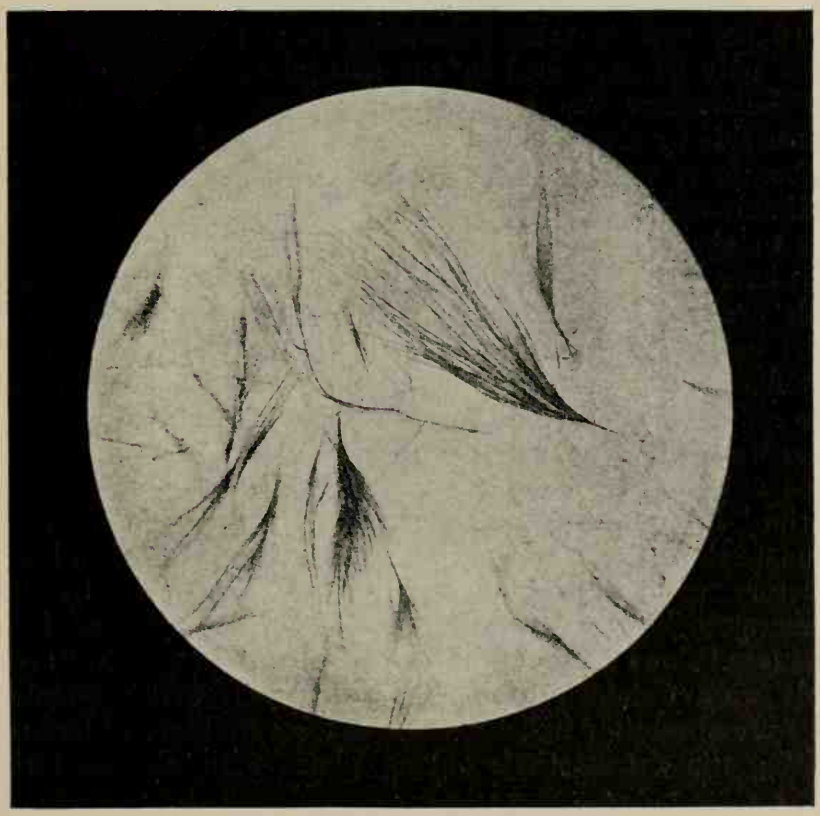

Fig. 10 —Beef Tallow Crystals. 50 diam.

Goske[1] stated at first that 5 per cent of beef fat, or 15 per cent of mutton fat (which does not crystallise so well), can be detected if the ethereal solution be allowed to crystallise at a temperature of 12°-13° C. But later he admits that the question becomes complicated if oleomargarine is substituted for beef stearine. Besides, German home-rendered lard did not yield the crystalline plates, crystallising as it did in needles which were not readily distinguishable from those yielded by beef stearine under the same conditions.

From the above observation it follows that examination under a low power of magnification should not be relied upon, but that examination under high powers is distinctly necessary. It should also be noted that if the plates lie on the narrow end, they may appear under the microscope as thin needles, thus leading to the confounding of lard crystals with beef crystals.

The author has further examined crystals obtained from the ethereal solution in *Stock's modus operandi* (see below) from (*a*) leaf lard, (*b*) lard from the shoulder, (*c*) lard from the loin, (*d*) lard from the back, (*e*) various pure American lards, and (*f*) mixtures of all the lards named with 5 per cent and 10 per cent of (1) beef tallow, (2) various brands of "beef stearine," and "oleostearine." All the observations confirm the result already stated, viz. that it would be very hazardous to declare on the strength of the appearance of the crystals under the microscope that adulteration with 5 per cent or 10 per cent of tallow or beef stearine or oleostearine had been practised. The statement made by several observers that it is possible to distinguish under the microscope a lard adulterated with 5 or 10 per cent of these substances from a pure lard can, in my opinion, only be explained by the natural bias of an observer who knows beforehand the composition of the sample. If he thus examines side by side samples of pure lard and of lard adulterated in the laboratory, then he does observe certain differences which are immediately ascribed to the influence of the adulterant. The proper way is to observe indiscriminately a large number of preparations, such as have been described above, without knowing beforehand what crystals are being examined. On proceeding in this manner a decision becomes very uncertain. In several cases even pure lards were judged by the author to contain some adulterant on the strength of the microscopical appearance, whilst some of the adulterated samples were decidedly declared as pure.

The author's conclusion that the microscopic appearance of the "stearine" from samples containing only 5 to 10 per cent of beef stearine must be regarded with the greatest circumspection, has found satisfactory confirmation in experiments carried out by *Dunlop*.[2] On recrystallising the "stearine crystals" as obtained in *Stock's* process (see below) from pure beef "stearine" and mutton "stearine," crystals were obtained after the third and fourth crystallisation which were absolutely indistinguishable from well-formed lard crystals exhibiting the characteristic oblong plates with oblique terminals.

[1] *Journ. Soc. Chem. Ind.* 1893, 469. [2] *Ibid.* 1906, 458.

In the third crystallisation the fine rods of mutton tallow gave place to thin plates, in many cases with oblique terminals as in lard

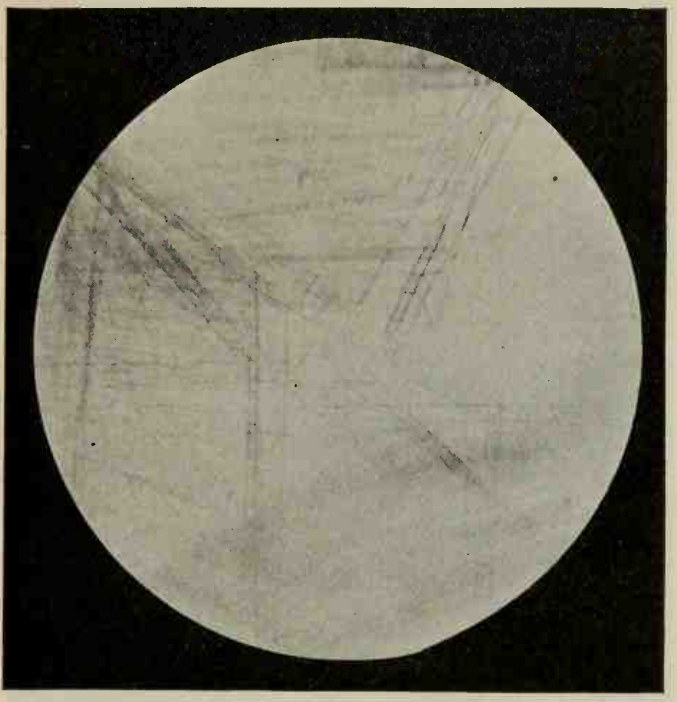

Fig. 11.—Mutton Stearine, 3rd Crystallisation 380 diam.

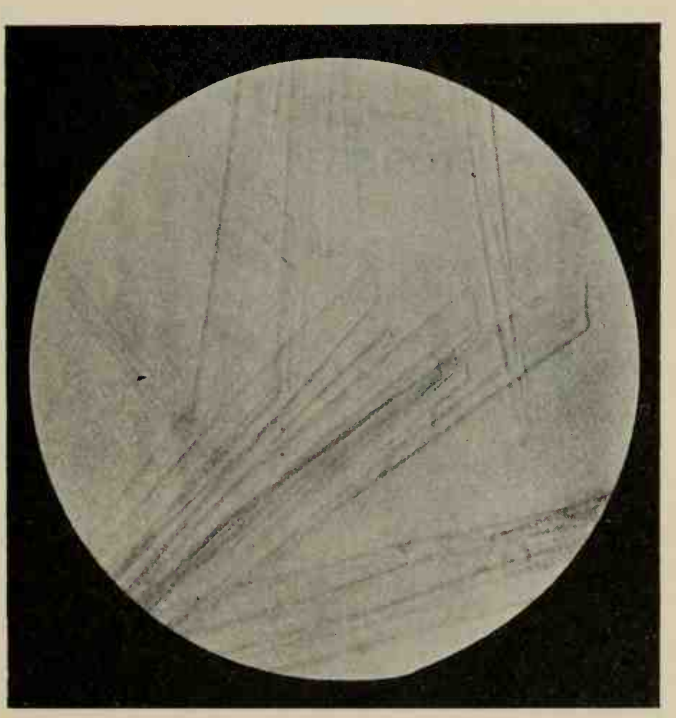

Fig. 12.—Beef Stearine, 3rd Crystallisation. 380 diam.

crystals at a magnification of 380. In the fourth crystallisation the lard form became already more distinct at a magnification of 100, and

even of 30 diameters. In the case of beef stearine, the crystals from the first crystallisation closely resembled those of mutton stearine.

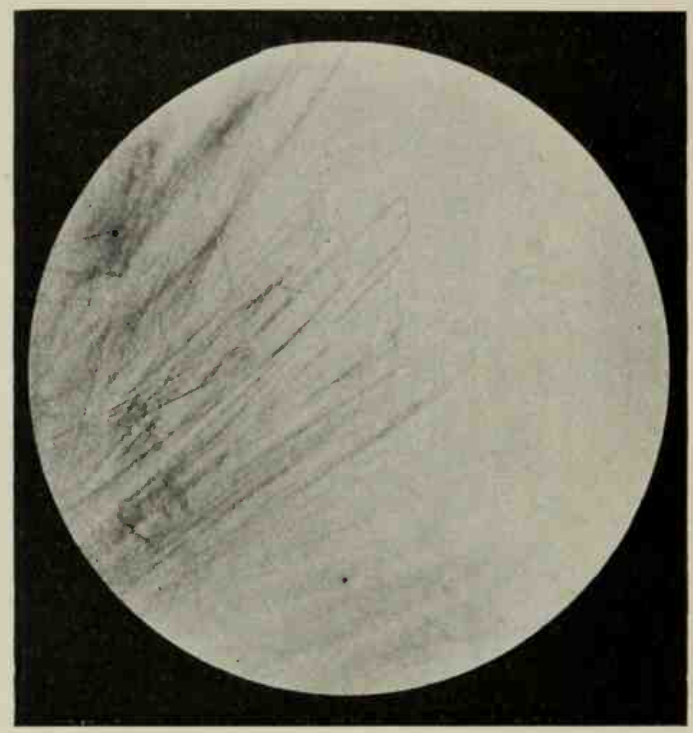

Fig. 13.—Mutton Stearine, 4th Crystallisation. 380 diam.

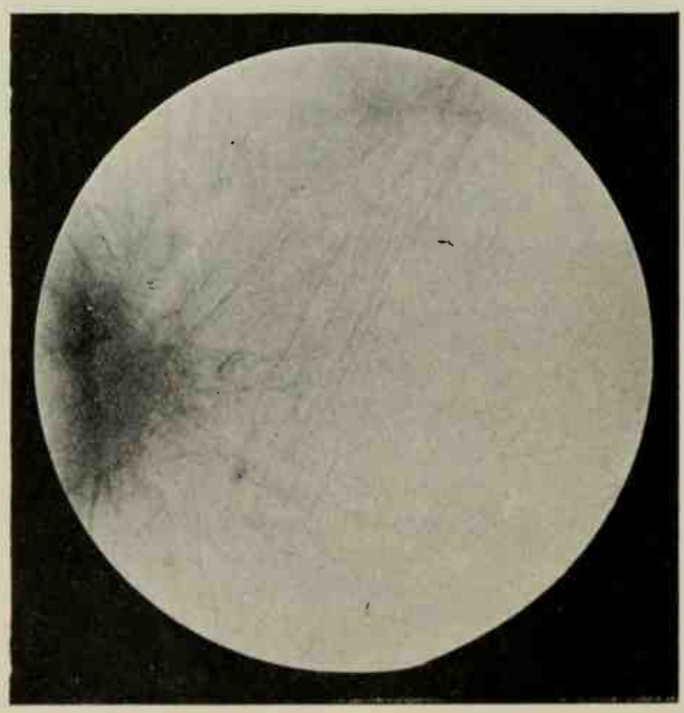

Fig. 14.—Beef Stearine, 4th Crystallisation 330 diam.

The second, and especially the third crops of crystals showed a decided change from beef to lard form at a magnification of 380,

whilst in the fourth crystallisation the chisel-shaped ends of the plates were clearly seen; at a magnification of 100 a number of groups were observed which had the appearance of "plumose" aggregates, but the individual crystals resembled lard plates more closely, and not the fine-pointed needles of beef crystals as seen in the first crystallisation. This will become apparent on examining the crystallisations illustrated by Figs. 11, 12, 13, 14 (due to *Dunlop*[1]). These observations distinctly controvert the statement made by *Hehner* and *Mitchell*[2] that crystals from "soft lards" (such as lard from the back) on being repeatedly recrystallised from ether become more and more needle-like, approaching the form of beef stearine crystals, until they become indistinguishable from them. A confirmation of this opinion was thought by these observers to be found in the increase of the percentages of stearic acid yielded by crystals obtained from three successive crystallisations of flare lard, they having found the following respective percentages of stearic acid:—32·4 per cent, 37·6 per cent, and 59 per cent. These numbers agree with the results obtained by *Kreis* and *Hafner* in a similar examination. Their numbers are reproduced in the following table:—

	Melting Point. °C.			Iodine Value.	Melting Point of the Fatty Acids. °C.	Stearic Acid. Per cent.
Original fat . . .			47-40	58·59	41-42	22·3
	1st Melting Point.		2nd Melting Point.			
1st crystallisation	48·0	and	62·0	11·95	56·0	57·5
2nd ,,	50·5	,,	64·2	1·11	59·5	66·8
3rd ,,	50·8	,,	64·5	0·21	61·0	67·2
4th ,,	51·4	,,	65·0	0·13	62·0	67·2
5th ,,	51·8	,,	65·8	0·14	...	...
6th ,,	51·8	,,	65·8	0·12	...	...

In conjunction with the last table there should be read the numbers recorded in the following two tables, giving the results of a corresponding examination of beef fat and mutton tallow:—

[1] *Journ. Soc. Chem. Ind.* 1906, 458. [2] *Analyst*, 1896, 328.

Beef Tallow

Melting Point. °C.				Iodine Value.	Melting Point of the Fatty Acids. °C.	Stearic Acid. Per cent.
Original fat . . .			43-44	35·8	44-45	39·5
	1st Melting Point.		2nd Melting Point.			
1st crystallisation	45·5	and	55·5	9·28	57·5	59·5
2nd ,,	47·0	,,	58·0	3·28	59·0	64·2
3rd ,,	48·5	,,	59·0	2·07	60·5	65·5
4th ,,	49·5	,,	59·8	1·30	62·0	66·4
5th ,,	50·0	,,	60·0	0·90	...	
6th ,,	50·0	,,	60·0	0·86	...	...
						...

Mutton Tallow

Melting Point. °C.				Iodine Value.	Melting Point of the Fatty Acids. °C.	Stearic Acid. Per cent.
Original fat . . .			45	42·5	42-43	35·5
	1st Melting Point.		2nd Melting Point.			
1st crystallisation	45·5	and	57·5	12·3	58·0	57·8
2nd ,,	47·0	,,	59·0	6·26	58·8	62·7
3rd ,,	50·5	,,	60·0	3·41	59·8	65·2
4th ,,	50·5	,,	60·8	3·00	62·2	67·0
5th ,,	51·0	,,	61·2	2·70	...	...
6th ,,	51·2	,,	61·5	2·65	...	...

It has been pointed out already that in the case of *lard from the loin* crystals were obtained which would appear to confirm the transition form of plates to needles. *Kreis* and *Hafner*, who were also unable to confirm *Hehner* and *Mitchell's* statement, expressed the opinion that the broad plates of lard (Fig. 9) consisted of heptadecyl distearin ("daturodistearin"), whereas hitherto only palmitodistearin and oleopalmitostearin had been obtained from tallow and beef "stearine." Since, however, it has been shown that heptadecylic acid is a mixture of several fatty acids, the more reasonable explanation would be that lard, tallow, and, consequently, beef and mutton stearine yield on repeated recrystallisation from ether one and the same glyceride, which crystallises in those oblong plates with oblique terminals which have hitherto been looked upon as solely characteristic of lard. The author finds a confirmation of his opinion in the following three tables which have been calculated by *Kreis* and *Hafner* from the three preceding tables. The iodine values found above

are converted into olein. By deducting the numbers so obtained from 100, the percentages given in the column "Olein-free-Fat" are found. The differences represent glycerides of saturated fatty acids, and the percentages of tristearin therein are calculated from the percentages of stearic acid.

Lard

	Iodine Value.	Olein. Per cent.	Stearic Acid.	Tristearin.	Olein-free Fat. Per cent.	Tristearin calculated to Olein-free Substance.
			Per cent of Fatty Acids.			
Original .	58·59	68·1	22·3	23·3	31·9	73·0
1st cryst. .	11·95	13·9	57·5	60·0	86·1	69·7
2nd ,, .	1·11	1·3	66·8	69·8	98·7	70·8
3rd ,, .	0·21	0·24	67·2	70·2	99·76	70·4
4th ,, .	0·13	0·15	67·2	70·2	99·85	70·3

Beef Tallow

	Iodine Value.	Olein. Per cent.	Stearic Acid.	Tristearin.	Olein-free Fat. Per cent.	Tristearin calculated to Olein-free Substance.
			Per cent of Fatty Acids.			
Original .	35·8	41·6	39·5	41·2	58·4	70·5
1st cryst. .	9·28	10·8	59·5	62·1	89·2	69·6
2nd ,, .	3·28	3·8	64·2	67·1	96·2	69·8
3rd ,, .	2·07	2·4	65·5	68·4	97·6	70·1
4th ,, .	1·30	1·5	66·4	69·3	98·5	70·3

Mutton Fat

	Iodine Value.	Olein. Per cent.	Stearic Acid.	Tristearin.	Olein-free Fat. Per cent.	Tristearin calculated to Olein-free Substance.
			Per cent of Fatty Acids.			
Original .	42·5	49·4	35·5	36·5	50·6	72·1
1st cryst. .	12·3	14·3	57·8	60·37	85·7	70·5
2nd ,, .	6·26	7·28	62·7	65·5	92·72	70·6
3rd ,, .	3·41	4·0	65·2	68·1	96·0	70·9
4th ,, .	3·00	3·5	67·0	70·0	96·5	72·5

It will be seen—and this has been pointed out already by *Kreis* and *Hafner* themselves—that in all three fats the percentages of saturated glycerides calculated to percentages of olein-free glycerides are the same. The increase in the percentage of stearic acid in the successive crystallisations is therefore due to the decrease of olein.

It further follows that the difference (if any) between the crystalline form of beef and mutton "stearines" on the one hand, and of lard crystals on the other cannot be conditioned by a difference in the percentage of stearic acid.

It should, however, be mentioned that *Kreis* and *Hafner* point out that the last crystallisations from beef fat (sixth and seventh) show distinctly the type of needles. This is at variance with *Dunlop's* observations; but since *Dunlop's* micro-photographs unmistakably prove his contention, whereas *Kreis* and *Hafner* have not published micro-photographs of the sixth or seventh crystallisation from beef fat, *Dunlop's* statement should be looked upon as carrying more weight. *Kreis* and *Hafner's* opinion may be explained by the fact that if the plates lie on their narrow side they may be easily mistaken for needles, although against this it must be pointed out that *Kreis* and *Hafner* themselves had observed that lard crystals when lying on the narrow side appear like finely-curved needles. Further experiments are therefore required to lead to a final decision between the conflicting statements.

Delafontaine's method consisted in dissolving lard in a mixture of alcohol and ether, allowing to stand twenty-four hours at a temperature of 12-15° C., and weighing the crystals which had separated.

Stock[1] combined the methods of *Belfield* and *Delafontaine*, and worked out more fully the quantitative determination of the "stearine." He compares the crystals obtained from an ethereal solution with those from two standard sets of mixtures; the first consisting of pure lard melting at 34°-35° C., with 5, 10, 15, and 20 per cent of beef stearine melting at 56° C.; the second of pure lard, of melting point 39°-40° C., with 5, 10, 15, and 20 per cent of beef fat melting at 50° C. *Stock* proceeds as follows:—The melting point of the sample is determined first by the capillary tube method. Suppose the melting point be found at 34° C., then 3 c.c. of the melted fat are run into a graduated stoppered cylinder of 25 c.c. capacity; 21 c.c. of ether, of specific gravity ·720, are added, and the fat dissolved at 20°-25° C. Three c.c. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to 13° C., and allowed to remain at that temperature or a lower one—particularly during the last hours—for twenty-four hours.

An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of deposited crystals. The ether is then poured off as far as possible, and 10 c.c. of fresh ether at 13° C. is added in each case. The contents of the cylinders are well shaken, cooled to 13° C., the proportion of crystals is read off, and the ether poured off as before. The operation is repeated, and the poured-off ether may be used for swilling the deposit out of the cylinders, but no fresh ether must be used. Finally, the contents of the cylinders are emptied into weighed shallow beakers, the ether

[1] *Analyst*, 1894, 2.

drained off carefully, the mass allowed to dry for fifteen minutes at 40° C., and weighed. The weight obtained for the sample under examination is compared with the weight of crystals obtained from whichever of the standards comes nearest to it.

The second set of mixtures is used for samples with a higher melting point.

The actual presence of beef fat should then be proved by microscopical examination, using a 1-inch objective and the C eye-piece.

Stock based his deductions as to the presence of beef stearine on experiments made with seven lards only. These were divided by him into two sets—the first embracing lards melting below 39° C., and the second, those melting above 39° C. No statement was made as to whether 39° C. defined the point when the lard had melted to a transparent liquid (see above).

Stock's data are reproduced in the following table :—

Melting Point.	Ether-washed Deposit. "Stearine."
°C.	Milligrams.
34	6
34·5	nil.
39	11
41·2	90
42·5	83
45·5	114
45·8	146

Basing himself on these results *Stock* laid down the rule that a lard of a "melting point" below 39° C., and yielding more than 11 mgrms. of "stearine," must be looked upon as adulterated with beef "stearine." The results of examinations made by the author, as also by *Dunlop*, prove that this generalisation is inadmissible. This will be gathered from the following table :—

[TABLE

"Stearine" (Ether-washed Deposit) from 3 c.c. of Lard

	Melting Points. °C.		Mgrms.	Observer.
	Commences to melt.	Completely melted.		
Lard from back of English hog	27·2	33·9	2·6	Lewkowitsch
Lard from loin ,,	33·9	42·8	36	,,
Lard from shoulder ,,	33·9	42·8	62	,,
Lard from the leaf ,,	38·3	47·8	178·2	,,
Pure "Bladder lard," No. 1	33·9	45	132·2	,,
Pure "Bladder lard," No. 2	35·6	45·1	136·4	,,
American lard	38·9	41·1	38·2	,,
English lard	30·0	41·1	68·2	,,
American lard	33·3	41·1	75·4	,,
,, ,,	30·0	43·3	70	,,
English lard from back	36		5	Dunlop
From leg	37		7	,,
From back	38		9	,,
From kidney bed	43		49	,,
From leaf	47		115	,,
From kidney bed	50		190	,,

Stock even claimed to be able to determine the amount of "beef stearine" present in an adulterated lard by recrystallising repeatedly the "stearine," on the assumption that "lard stearine" is more readily soluble in ether than "beef stearine." The finally obtained "stearine" was then looked upon by him as "beef stearine" and calculated to the amount of adulterant added. *Dunlop* has, however, shown by exact experiments that the "stearine" from beef fat, obtained by a single crystallisation, is actually more soluble in ether than the "stearine" from the first crystallisation of lard. Any attempt to calculate the amount of "beef stearine" from the recrystallised "stearine" must, therefore, lead to failure.

Cochran[1] uses fusel oil for the preliminary separation of stearine crystals, which he then examines by the *Belfield-Stock* method. He proceeds as follows:—2 c.c. of the melted fat are placed in a stoppered cylinder graduated for 25 c.c., and 22 c.c. of fusel oil are added. The contents of the cylinder are slightly warmed to effect complete solution, and gradually allowed to cool to 16°-17° C., at which temperature they are kept for two to three hours. The deposited crystals are filtered off, dissolved in ether, allowed to crystallise out as described above, and finally subjected to microscopical examination. *Cochran* claims that smaller proportions of beef fat can thus be detected than by the above described methods, but it must be open to doubt whether his method yields better results than the one previously described.

[1] *Journ. Soc. Chem. Ind.* 1898, 74.

In the present state of our knowledge[1] *Stock's* modification of *Belfield's* method must be considered the best, provided it be used with circumspection such as is dictated by the numbers given in the last table and in the following table :—

"Stearine Crystals" obtained from Beef Stearine and Mixtures thereof with Lard by Stock's "Modus Operandi" (Lewkowitsch)

	Melting Point.		Mgrms.
	Commences to melt.	Completely melted.	
	At °C.		
Beef stearine . . .	52·7 –	52·8	1503·0
Leaf lard[2] containing 5 per cent tallow . . .	42·2 –	47·8	171·6
Leaf lard[2] containing 5 per cent beef stearine .	44·4 –	47·2	216
Leaf lard[2] containing 5 per cent oleostearine .	43·3 –	47·2	207
Leaf lard[2] containing 10 per cent tallow . .	31·1 –	48·3	165·6
Leaf lard[2] containing 10 per cent beef stearine .	42·8 –	47·8	260
Leaf lard[2] containing 10 per cent oleostearine .	40·6 –	47·8	278·4
American lard[3] containing 5 per cent beef stearine	30·0 –	46·7	267·4
American lard[3] containing 5 per cent oleostearine	33·9 –	39·4	197·8
American lard[3] containing 10 per cent beef stearine	30·0 –	39·4	189·6
American lard[3] containing 15 per cent beef stearine	...	...	263·4
American lard[3] containing 20 per cent beef stearine	...	...	365
American lard[3] containing 30 per cent beef stearine	...	...	502·8

It will be observed that, curiously enough, the added amount of tallow reduces the quantity of stearine found (an observation which has also been made by *Dunlop*); for a lard yielding 178·2 milligrams of "stearine" gave, after being adulterated with 5 and 10 per cent of tallow, 171·6 and 165·6 milligrams respectively. In the case of an addition of 5 per cent of tallow to a "hard" lard, neither

[1] A curious method to detect and determine the quantity of beef fat in lard was proposed by Balló, viz. to measure the amount of air enclosed in the melted fat; pure lard on solidifying is stated not to enclose any air, whereas pure beef fat encloses air (100 grms. about 6·5 to 8·8 c.c.). Balló is of the opinion that even 3 per cent of beef fat may be thus detected (*Journ. Soc. Chem. Ind.* 1897, 764).

[2] Sample No. 4 of preceding table yielding 178·2 mgrms. of "stearine."

[3] Sample No. 10 of preceding table yielding 70 mgrms. of "stearine."

the amount of stearine, nor the melting point, nor even the microscopic appearance would lead to a safe conclusion.

The examination of the crystals under the microscope should, however, never be omitted.

If a "soft" lard has been adulterated with 10 per cent of oleostearine, the indications furnished by the melting point and the amount of stearine, combined with the microscopical appearance, will assist in coming to a conclusion. In such a case the author observed a number of aggregates of the "plumose" form, which even under a high power of magnification were not resolved into plates.

Further research is required to solve the problem of detecting with certainty in every case 5 per cent or 10 per cent of beef stearine in lard.[1] The methods which the author suggested in the last edition of this work, viz. the determination of stearic acid and the determination of "daturic acid," are unable to solve the problem satisfactorily in every case.

If by examination of the mixed fatty acids the statement should be confirmed that lard differs essentially from tallow, in that it contains notable amounts of myristic acid (which is practically absent from tallow), then the fractional distillation of the methylesters might lead to a decision. It should be pointed out that the author has not tested the value of this suggestion by experiments.

In case lard has been adulterated with both beef stearine and a vegetable oil,—in other words, if a "compound lard" is under examination,—then the phytosteryl acetate test alone furnishes the safest information. If it then should be desired to determine the amount of tallow or beef stearine, resort should be had to *Wesson's* cooling test (cp. Vol. III. Chap. XV. "Lard Substitutes").

In connection with the manufacture of lard there are produced as secondary products—

(*a*) Lard stearine.
(*b*) Lard oil.

These two products are manufactured from prime steam lard by allowing it to crystallise at a carefully regulated temperature—in winter from 45° to 55° F., and in summer from 55° to 65° F.—so that the stearine may separate as a crystallised mass, ready to part with the lard oil when subjected to pressure (cp. Vol. III. Chap. XV. "Margarine"). If no proper crystallisation takes place, it is impossible to express the oil, as the whole material passes through the cloths ("spues") (cp. "Demargarinating process," p. 32). The crystallised mass is wrapped in cloths—in small works by hand, in large works on rotating packing tables. In small establishments lever presses are in use almost exclusively. The lever press is much

[1] Cp. also Soltsien, *Chem. Revue*, 1908, 103; Seitter, *Zeit. f. Unters. Nahrg. u. Gen.* 1908, xv. 485.

in vogue for the preparation of a high-class lard oil, for the preparation of which the pressure must be applied slowly. In large establishments automatic mechanical or hydraulic presses are employed.

The cakes remaining in the press are sold as lard stearine (French—*Saindoux pressé, Solar stéarine*; German—*Solarstearin*).

(*a*) **Lard stearine** is used in the manufacture of compound lard and—chiefly in Europe—for "stiffening" soft lard. In the United States it is also used in the manufacture of margarine ("oleomargarine"). (See Appendix.)

Lard stearine from lard unfit for edible purposes is autoclaved and converted into candle material.

(*b*) **Lard oil** (French—*Huile de lard*; German—*Schmalzöl*; Italian —*Olio di lardo*), if obtained from the best neutral lard, is used as an ingredient in the manufacture of margarine, etc. Lower qualities are employed as high-class burning and lubricating oils.

According to the pressure and the temperature employed in the process of separating the liquid from the solid portion, the solidifying point of lard oil varies, so that some specimens will deposit "stearine" at the ordinary temperature, or even solidify completely at 10°-12° C., whereas others do not deposit any crystals unless cooled to the freezing point. Hence the usual characteristics, such as the specific gravities, and especially the iodine values of different lard oils, vary considerably, as is evidenced by the numbers contained in the following table :—

Physical and Chemical Characteristics of Lard Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Butyro-refracto-meter.	
At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At 40° C. "Degrees."	Observer.
15	0·916	Duyk[1]	193	Duyk	73	Duyk	0	Duyk	47	Duyk	41	Duyk
15·5	0·915	Allen			67-79[3]	Schweitzer and Lungwitz						
18	0·9137	Long										
20	0·9122	,,			80-82	Dupont						
25	0·9088	,,			69·7-75·9	Tolman and Munson						
30	0·9053	,,			70-75[2]	Voigtländer						
35	0·9019	,,			88[3]	,,						
100	0·8626	Duyk										

Iodine value of the liquid fatty acids, 94·0 to 95·8 in European lard oils ; 106 to 109 in American lard oils (*Lewkowitsch*).

[1] *Bull. Assoc. Belge des Chim.* 1901, 590. [2] European. [3] American.
[4] Cp. also *Journ. Amer. Chem. Soc.* 1903, 966.

Tolman and *Munson*[1] found in a number of lard oils from 18·9 to 26·7 per cent of solid fatty acids by the lead-salt-ether method.

In the elaïdin test lard oil behaves very much like olive oil.

The change which lard oil undergoes on blowing with air at 100° C. is characterised by the numbers given in the following table[2]:—

Blown. Hours.	Specific Gravity.	Refractive Index.	Iodine Value.
0[3]	0·914	1·4697	78·0
3	0·917	1·4699	76·0
6	0·917	1·4700	75·0
9	0·917	1·4705	72·0
12	0·918	1·4707	72·0
15	0·920	1·4708	71·0
18	0·923	1·4709	67·0
21	0·923	1·4710	67·0
24	0·925	1·4713	66·0

Lard oil is a water-white to pale yellow liquid at the ordinary temperature. If made from fresh steam lard it is practically devoid of free fatty acids. Such lard oil is used (chiefly in Europe) in the manufacture of compound lards and in the manufacture of margarine ("oleomargarine"). Those lard oils which are unsuitable for edible purposes and contain a small amount of free fatty acids are used as high-class lubricating oils, wool oils, finest burning oils, and in the United States in place of olive oil for making silk-scouring soaps, and for lubricating the silk fibre for weaving.

On account of its high price, lard oil is very frequently adulterated.

Adulterants, such as mineral oils or vegetable oils, are detected by the quantitative reactions and the methods described above. Fish and blubber oils in lard oil intended for lubricating purposes are best detected by isolating the ether-insoluble bromides of the liquid fatty acids.

BEEF MARROW FAT

French—*Graisse de moelle de bœuf.* German—*Rindermarkfett.*
Italian—*Grasso di midollo di bove.*

For tables of characteristics see p. 618.

Beef marrow fat is recovered from the marrow bones of cattle. The marrow fat from the shin bones is, in the United States, usually put together with the oil from the feet (cp. "Neat's Foot Oil").

[1] *Journ. Amer. Chem. Soc.* 1903, 966.
[2] Procter and Holmes, *Journ. Soc. Chem. Ind.* 1905, 1287.
[3] Original oil.

Physical and Chemical Characteristics of Beef Marrow Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index. Butyro-refracto-meter.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	"Degrees" at 25° C.	Observer.
0·9311-0·938	Zink	31-29	Zink	37-45	Zink	199·6 195·8-198·1	Lewkowitsch Zink	55·4 39·2-50·9 52	Lewkowitsch Zink Dunlop [1]	1·1	Zink	55·3	Dunlop

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9300-0·9399	Zink	37·9-38 [2] 40-39	Lewkowitsch Zink	45-46 [3]	Zink	204·5	Zink	55·5	Lewkowitsch

[1] *Analyst*, 1907, 318. [2] Titer Test. [3] Capillary Tube Method.

Medullic acid, stated by *Eylerts* to occur in beef marrow, is, according to *Thümmel*, a mixture of palmitic and stearic acids.

Freshly rendered marrow fat has a low acid value, 0·44 (*Dunlop*[1]), 1·6 (*Zink*). A specimen eight months old gave the number 1·9. Evidently the acid value depends on the state of freshness of the bones. According to *Glikin*[2] iron seems to occur regularly in beef marrow fat; the marrow of young animals is stated to contain a higher amount of iron than that of old animals.

Nerthing[3] examined separately beef marrow fats from red and yellow marrow. The fat from yellow marrow is stated to consist of 78 per cent of oleic acid, 14·2 per cent of stearic acid, and 7·8 per cent of palmitic acid; and the fat of red marrow of 47·4 per cent of oleic acid, 36·3 per cent of stearic acid, and 16·3 per cent of palmitic acid. The yellow marrow contained 0·3 per cent of cholesterol and 0·18 per cent of lecithin, and the red marrow 0·28 per cent of cholesterol and 0·2 per cent of lecithin.[4]

Beef marrow fat is used in pharmacy and for making pomades.

BONE FAT

French—*Suif d'os.* German—*Knochenfett.*
Italian—*Grasso d' ossa.*

For tables of characteristics see p. 622.

Bone fat is practically a by-product in the process of working up bones, whether they be intended for the manufacture of char or for the production of glue and gelatine. In either case the "degreasing" of the bones must precede all further manipulations. Bones from heads, ribs, shoulder blades, etc., contain from 12 to 13 per cent of fat, whilst the large thigh bones ("marrows") contain as much as 18 to 20 per cent. These numbers apply to fresh bones only. The amount of fat that can be recovered decreases according to the age and rancidity of the bones. Bone fat is obtained chiefly by two processes—firstly by boiling with water at the ordinary pressure, or by steaming under high pressure; and secondly, by extracting with volatile solvents.

The oldest process for producing bone fat consisted in boiling the broken bones with water in open vessels and allowing the hot liquor to stand, when the fat separating on the top was skimmed off. If fresh bones were used, the bone fat so recovered had a white to yellowish colour, a faint odour and taste, and possessed the consistence of butter.[5] If, however, old and putrid bones were employed, the bone fat so recovered passed, according to the age and state of decomposition of the organic matter in the bones, through all gradations, from white fat (containing a few per cent of free fatty

[1] *Analyst*, 1907, 318.
[2] *Berichte*, 1908, 910.
[3] *Biochem. Ztschr.* 1908, 167.
[4] Cp. *ibid.* 1907, 235.
[5] In the United States bone fat of this description is sold under the name "butterstock-tallow."

acids and an inconsiderable amount of impurities, and having a slightly disagreeable smell) to a brownish, less pleasantly smelling fat, and finally to a dark brown mass of offensive odour. This last contained large quantities of free fatty acids, lime soaps (formed by the action of fatty acids on the lime salts of the bones), and, furthermore, calcium salts of lactic acid and of volatile fatty acids (such as butyric, etc.), which are the usual concomitants of rancidity.

By this boiling-out process only half of the fat contained in the bones can be recovered.

Not only was the yield an inferior one, but the nuisance created by the evil smells emitted from bone works has rendered this process a practically obsolete one.

An important improvement in the manufacture consists in treating the bones with steam under pressure. The bones are broken and placed in a cage fixed inside an autoclave, where they are heated with open steam under a pressure of two or three atmospheres. The bone fat resulting from this process is of the same quality as the fat obtained by the obsolete process, especially if the steaming is limited to the shortest possible time, so that only a small amount of glue-yielding material is extracted. In large slaughter houses, especially those of America (United States and South America), where the bones are worked up in the fresh state, the boiling or steaming out is preceded by a washing operation in "bone-washing machines." These are cylinders usually 10 feet long and 3 feet to 4 feet in diameter, built up from iron bars, 1 inch apart, fixed into two cast-iron heads. They are driven by chain and sprocket and rotate slowly, making about ten revolutions per minute. Through the entire length of the drum there is a hinged door made of bars, which allows the filling and emptying of the cylinder. The machines are usually set at an angle to facilitate the washing and emptying operations. Some manufacturers even resort to steeping the bones in a solution of sulphurous acid in order to obtain a whiter fat (as also a better glue). The yield of bone fat in the steaming-out process under pressure is considerably higher (by about 50 per cent) than in the boiling-out process in open vessels, so that from bones containing 12 per cent of fat, about 8 to 9 per cent can be recovered.

Bone fats of this quality can be bleached, but only the best kinds are likely to yield a good product. The higher the percentage of free fatty acids, the greater is the difficulty in bleaching. In fact, products containing more than 50 per cent of free fatty acids could not hitherto be bleached successfully.

Practically the total amount of bone fat in bones can be obtained by treatment with solvents, a process which leaves the animal tissue unimpaired, so that the whole of the glue-yielding organic substances can be converted into glue after the fat has been removed. Hence the *extraction process* has come largely into vogue. Especially those bones which are no longer fresh are worked up in this manner. The solvents used for extraction were up to recently

almost exclusively petroleum ether (benzine) and Scotch shale oil, (boiling between 212° and 270° F.). Latterly also carbon tetrachloride has been used on an experimental scale.

The extraction with *benzine* or *shale oil* takes place in iron digesters under pressure, or in open apparatus. The process in which pressure is employed is the more dangerous one, and has not infrequently led to explosions. The yield depends on the time during which the solvent acts on the bones, as also on the construction of the apparatus used. That apparatus will be the best in which the volatile solvent is so successfully condensed that only a small amount is lost. The fat obtained by the extracting process is dark brown, and has a very penetrating, unpleasant smell. This fat contains besides a considerable amount of free fatty acids, lime soaps, calcium lactate, calcium butyrate, hydrocarbons from the petroleum ether, and colouring substances. Hitherto this kind of fat has not been bleached successfully, and even when some immediate improvement was obtained, the colour, as also the unpleasant smell, "reverted" after a short time.

The extraction by means of carbon tetrachloride is carried out in open vessels; as the solvent attacks iron, the vessels must be lead-lined. Specimens of carbon tetrachloride-extracted bone fats, which the author has had occasion to examine, were superior as regards smell and colour to benzine-extracted fats (cp. p. 22). This may be ascribed to the fact that carbon tetrachloride permits a lower temperature to be employed; at such lower temperature the organic nitrogenous substances are less attacked than is the case if the higher boiling benzine is used. Hitherto the price of this solvent has militated against its introduction in bone fat works, and carbon tetrachloride-extracted bone fat has not yet been placed on the market in considerable quantities.

The following statistical data may be of interest:—

Import of Bones into Germany (in Tons) during 1902-1906

Origin.	1902.	1903.	1904.	1905.	1906.
La Plata . . .	1759	3696	253	1250	...
Levant . . .	2202	1104	1375	1909	710
Other countries . .	858	783	1079	938	640

Whereas bone fat obtained by the boiling and steaming-out processes can be used for soap making, bone fat extracted by means of benzine is utterly unsuitable for that purpose in this country on account of its rank odour, and can only be used in candle works. On the Continent such benzine-extracted fat does find employment in small quantities for inferior soaps. If bone fat intended for soap-making purposes contains a considerable amount of lime, it is treated with dilute mineral acid.

Physical and Chemical Characteristics of Bone Fat [1]

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
At 15·5° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·914-0·916	Allen	15 rising to 17	Schaedler	21-22	Schaedler	190·9	Valenta	46·3-49·6	Wilson
...	...	...	...	...	...	194-195 [1]	Lewkowitsch	48-55·8	Valenta

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
28	Hübl	30	Hübl	57·4 [2]	Morawski and Demski	200	Valenta
...	...	...	...	55·7-57·3 [3]			

[1] Prepared by boiling out fresh bones. [2] Crude fat. [3] Refined fat.

Occasionally bone fat is worked up for the preparation of "bone oil" (cp. also "Neat's Foot Oil"). The process is exactly the same as that employed in the production of tallow oil (see p. 634). "Bone oil" is used as a lubricant, and in the leather industries in a similar manner to neat's foot oil. If practically devoid of free fatty acids, it represents one of the finest lubricating oils on account of its low "cold test."

The chemical composition of bone fat lies between that of marrow fat and tallow. Hence the valuation of bone fat is carried out in a similar manner to that of tallow. But a complication arises through the presence of calcium salts of higher fatty acids, and of calcium lactate and butyrate.

It has been pointed out already (Vol. I. Chap. IV.) that lime soaps tenaciously retain water, so that the direct determination of moisture may lead to erroneous results. With regard to impurities of a non-fatty nature, it should be borne in mind that different results are obtained according as the fat is extracted after previous drying (as in the English or German method), or is extracted undried (as in the French method). From dried bone fats most of the lime salts are dissolved by petroleum ether, whereas in the case of undried bone fats most of the soaps remain undissolved. The method employed should, therefore, be distinctly stated when the results of the analysis are returned.

The errors inherent to the older methods are avoided by adopting the process proposed by *Shukoff* and *Schestakoff*[1]:—

Fatty Matter.—This is determined direct. Weigh off 10 grms. in a small conical flask, add 3 to 5 drops of strong hydrochloric acid, and warm on the water-bath for about 1 hour, agitating the contents of the flask from time to time, whereby the lime soaps are decomposed. Then add 40 c.c. of petroleum ether, agitate to dissolve the fatty matter, and pour the solution carefully (leaving the few drops of acid at the bottom of the flask) through a tared filter into a second flask; wash two or three times with petroleum ether, and determine the fatty matter in the ethereal solution as described Vol. I. Chap. IV.[2]

Impurities, organic and inorganic.—The dirt and the acid solution from the first flask are washed on to the tared filter, dried, and determined as described Chap. IV.; of course, lime and other inorganic substances are washed away with the acid solution.

Ash.—This is found by incinerating a fresh portion of the sample. The lime of the organic lime salts is thus converted into calcium carbonate; the amount of the latter may be ascertained by titrating the ash with standardised acid.

Moisture.—This is found by difference (cp. also p. 640).

The fatty matter consists of the neutral fat, of the free fatty acids originally contained in the bone fat, and of fatty acids liberated from the lime salts. It also contains, of course,

[1] *Chem. Rev.* 1898, 6.

[2] Cp. also Schicht and Halpern, *Chem. Zeit.* 1907, 279.

unsaponifiable matter. Among the latter *Shukoff* and *Schestakoff* found cholesterol to the extent of from 0·2 to 0·6 per cent. The amount of the unsaponifiable matter is found by the method described in Vol. I. Chap. VI.

The determination of the unsaponifiable matter is of great importance, as during the last few years admixture to bone fat of all kinds of waste fats, especially of those containing considerable amounts of unsaponifiable matter (see Vol. III. Chap. XVI. "Waste Fats"), has been practised to a considerable extent. The examination of the isolated unsaponifiable matter is frequently required, and is carried out by the method given in Vol. I. Chap. IX. Adulteration with wool fat—said to occur in continental bone fats—would thus be readily detected.

The following table reproduces some analyses published by *Shukoff* and *Schestakoff*:—

Description of Bone Fat.	Fatty Matter.	Impurities.		Moisture by Difference.	Unsaponifiable Matter.	Titer Test.
		Organic.	Inorganic.			
	Per cent.	Per cent.		Per cent.	Per cent.	°C.
Russian—Petersburg .	98·65	0·15		1·20	1·80	39·9
,, .	99·00	0·15		0·85	0·82	39·9
,, .	99·10	0·10		0·80	0·52	40·2
Russian	99·15	0·10		0·75	0·50	42·5
,, ...	97·30	0·10	0·40	2·47	1·07	40·3
,, ...	96·60	0·05	0·50	3·58	1·12	39·1
,, from the South .	94·35	0·25	0·90	4·50	1·40	41·4
,, ,, .	92·45	0·30	0·70	6·55	1·20	40·9
,, ,, .	93·35	0·08	0·20	6·37	1·26	39·7
English—pale . .	98·20	0·25	0·75	1·42	0·56	39·3
,, "melted stuff"	97·04	0·30	0·15	2·15	...	39·8

The following two tables contain some analyses of bone fats. The first table is due to *Valenta*,[1] the second to *Troicky*[2]:—

[1] *Zeit. f. chem. Industrie*, 1887, 265; *Jour. Soc. Chem. Ind.* 1888, 219.
[2] *Chem. Zeit.* 1890, Rep. 239.

[TABLE

Bone Fat.	No.	Water.	Fatty Acids.	Free Fatty Acids.	Melting Point of Fatty Acids.	Neutralisation Value. Fatty Acids.	Iodine Value of Fatty Acids.	Ash.	Remarks.
		Per cent.	Per cent.	Per cent.	°C.			Per cent.	
Extracted .	1	6·31	89·8	25·8	41·5	206	52·1	1·35	Very impure, nearly black, smell unpleasant.
,, .	2	2·20	93·7	...	42·3	204·5	50·9	1·85	Brown.
,, .	3	2·55	91·5	18·7	41·7	205	51·3	2·01	...
,, .	4	...	...	...	42·0	205	48	...	Fatty acids obtained from No. 1 by distillation.
,, .	5	1·7	93·5	26·5	41·5	200	51·3	1·3	Rather dark.
,, .	6	1·33	...	24·6	41·5	206·1	55·8	0·11	...
,, .	7	...	92·9	18·4	41·8	205·8	52·8	...	Very dark.
,, .	8	...	92·3	20·1	42·0	205	...	...	...
Boiled out	9	...	...	...	45·1	201	44·3	...	Fatty acids from marrow bones, prepared in laboratory.
,, .	10	...	...	...	33·5	208·1	75	..	Fatty acids from horse marrow bones, prepared in laboratory.
,, .	11	2·05	90·4	14·8	41·5	207	53·5	...	...
,, .	12	3·08	90·7	21·9	41·7	206	52·8	...	...

No.	Description of Bone Fat.	Water.	Ash.	Fatty Acids.	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids.	Oleic Acid.	Stearic Acid.
		Per cent.	Per cent.	Per cent.			°C.	Per cent.	Per cent.
1	Boiled out . .	1·20	0·31	93·20	187·0	57·2	39·0	59·18	34·02
2	,, .	0·47	0·94	94·40	194·3	56·0	40·2	58·69	35·71
3	Extracted .	0·58	0·56	94·12	193·8	52·0	40·9	54·34	39·78
4	Boiled out, Russian	0·84	2·40	86·10	172·0	50·3	42·65	48·08	38·02
5	Extracted, ,, .	0·78	1·25	91·30	188·7	51·5	40·75	52·20	39·10
6	,, . .	0·85	1·76	91·00	181·0	54·8	40·0	55·36	35·64
7	,, . .	1·82	1·52	92·40	185·6	55·8	40·1	57·24	35·16
8	,, . .	0·91	1·06	92·85	187·0	55·2	40·9	56·90	35·95
9	Boiled out, from horse bones	1·52	1·82	91·50	184·0	62·7	36·1	63·69	27·81

For other kinds of bone fat, see Vol. III. Chap. XVI. "Bone Grease."

As has been pointed out already, bone fat is worked up in soap and candle works. It has also been mentioned that the benzine-extracted fat is practically unusable in soap-making. Such bone fat forms suitable material for candle-making purposes. The "stearine" ("stearic acid") obtained from bone fat crystallises readily, but on account of its inferior properties as a candle material bone fat is not worked up by itself (Vol. III. Chap. XV.) for candles, but generally in admixture with other raw materials. The impurities contained in bone fat, notably the fatty acids of low molecular weight, pass into the glycerin waters. They are liable to ferment, and the crude glycerin finally obtained contains impurities which are not readily removable even by distillation. Dynamite glycerin made from such raw material not infrequently contains trimethyleneglycol (see Vol. III. Chap. XV.).

TALLOW [BEEF TALLOW, MUTTON TALLOW]

French—*Suif* (*de bœuf, de mouton*). German—*Talg* (*Rindstalg, Hammeltalg*). Italian—*Sego* (*di bove, di montone*).

In commerce a distinction is made between *beef tallow* and *mutton tallow*. The former is obtained from oxen, cows, and calves; the latter from sheep and goats. This distinction is, broadly speaking, supported by chemical differences in the composition of the respective triglycerides, mutton tallow being as a rule richer in stearin than beef tallow (see below).

The quality—especially the hardness—of tallow depends on the breed and the age of the animal, and to some extent on the food. The fat from the male beast is generally harder than that obtained from the female. Animals fed on grass yield a harder fat than those fed with oilcakes; brewery refuse produces especially soft tallow. Hence we have all gradations, from the hard South American beef tallow to home-melt tallow of somewhat softish consistence.

The rough fat is delivered with the adhering tissue, etc., to the tallow-melters, and is rendered at a temperature of about 100° C. or above, as has been described already (p. 3).

The fats from different parts of the carcase, although of unequal value, are not kept separate, unless the fat be intended for the manufacture of oleomargarine, or of best commercial quality.

At present the tendency prevails to collect the rough fat, as far as possible, in large rendering establishments fitted up with modern appliances. Hence the slaughter-houses in large towns—especially on the Continent—have at present as an adjunct a tallow-rendering establishment. These are found on the most gigantic scale in the large packing-houses of the United States of America as also of South America.

For the production of tallow for the manufacture of margarine the more valuable kidney fat ("suet") and bowel fat ("midgerum fat") [French—*Suif en branches* or *en rames*; German—*Rohkern*] is dealt with separately and not mixed with the caul- (or kell-, i.e. *omentum*) fat [French—*Dégraisse*; German—*Rohausschnitt*].

By melting this selected fat at low temperatures—not exceeding 50° C.—the "premier jus" is obtained (cp. Vol. III. "Margarine").

The production of "premier jus" and the further working up of the same into "beef stearine" (or "mutton stearine") and oleomargarine, "oleo oil," is carried out on practically the same lines as described under the heading "Lard." Fuller details are given in Vol. III. under the heading "Margarine."

The following commercial brands of tallow are differentiated :—

(1) Rendered tallow, which contains all the fat from the carcase.

(2) "Premier jus."

(3) Pressed tallow (tallow stearine, beef stearine, mutton stearine, oleostearine).

(4) Oleomargarine, oleo oil.

The first-named quality of tallow, viz. "rendered tallow," is frequently expressed in hydraulic presses for the preparation of tallow stearine and tallow oil (see below).

It is almost impossible to estimate the quantity of home-melt tallow produced in European countries, as the production is scattered over the smallest establishments embracing even those of butchers in villages. The amount of home-melt tallow produced depends, of course, on the stock of cattle and sheep kept in each country. From carefully collected private information the author estimated that the production of home-melt tallow of the United Kingdom in 1900 represented a value of £3,000,000 (corresponding to over 100,000 tons). This seems to have increased in the year 1902 by about 10 per cent. But no absolute reliance can be placed on these figures, and it would rather appear from official publications that the amount is decreasing, for whilst the number of cattle kept in this country in 1871 amounted to 9,320,000 heads, and had increased to 11,504,000 in 1900, the number of sheep had actually decreased from 33,192,000 heads in 1871 to 29,746,000 in 1900. This is further confirmed by the following numbers taken from the "Agricultural Returns of Great Britain." The returns were collected 4th June 1907, and are compared with the same returns for 1906 :—

	Cattle.		Sheep.		Pigs.	
	1906.	1907.	1906.	1907.	1906.	1907.
	Heads.	Heads.	Heads.	Heads.	Heads.	Heads.
England . .	5,060,862	4,988,183	14,839,927	15,099,976	1,983,602	2,257,178
Wales . . .	747,715	738,884	3,586,095	3,703,372	209,660	232,996
Scotland . .	1,202,279	1,185,452	6,994,338	7,313,155	130,199	146,634
Total for Great Britain .	7,010,856	6,912,519	25,420,360	26,116,503	2,323,461	2,636,808

An approximate estimate as to the amount of "home-melt" tallow that is obtained from imported living animals may be derived from the numbers reproduced in the following table :—

Heads of Imported Living Animals (*Exports and Re-exports deducted*)

	1903.	1904.	1905.	1906.	1907.
Oxen and Bulls . . .	518,435	545,005	560,202	555,544	463,047
Cows	1,411	1,138	796	...	3,687
Calves	...	...	80	1	143
Sheep and Lambs . .	348,660	374,098	174,706	90,643	95,534

Corresponding returns for other countries, as far as they are available, are collated in the following table :—

[TABLE

	Cattle.		Sheep.	
	Year.	Heads.	Year.	Heads.
France	1893	12,879,000	1862	29,500,000
	1904	14,137,000	1882	23,800,000
	...	...	1900	20,180,000
	...	...	1904	1,780,000
Germany	1873	15,777,000	1873	25,000,000
	1883	15,787,000	1883	19,190,000
	1900	18,391,000	1892	13,590,000
	1904	18,940,000	1900	10,865,000
	...	...	1904	9,690,000
Austria	1891	8,644,000	1868	5,025,000
	1900	9,511,000	1880	3,841,000
	...	...	1901-4	2,621,000
Hungary	1884	4,879,000	1870	15,076,000
	1895	6,738,000	1880	9,389,000
	...	...	1901-4	8,122,000
Russia	1883 [1]	46,725,000	1870 [1]	45,297,000
	1900	43,587,000	1882 [1]	47,509,000
	1904	33,710,000	1901-3	70,647,000
	...	...	1904	53,185,000
Algeria	1870	725,000	1870	4,919,000
	1881	1,112,000	1881	5,995,000
	1890	1,233,000	1890	8,952,000
	1900	992,000	1900	6,723,000
	1904	1,080,000	1904	8,611,000
United States of America .	1890	52,802,000	1890	43,431,000
	1900	43,902,000	1900	41,883,000
	1904	61,242,000	1904	45,870,000

None of the European countries are at present exporting tallow, the quantities exported from the United Kingdom being in fact re-exports. Russia, which up to about two decades ago was a tallow-exporting country, has been forced to draw upon the world's supply for her own demands.

The chief sources of tallow—in addition to the "home-melt" production—are at present Australasia, South America, and North America. The quantities imported into the United Kingdom and the surplus exported to the Continent of Europe are given in the following table:—

[1] The provinces of the North Caucasus are not included.

Imports of Tallow into, and Exports from, the United Kingdom

Import of Tallow.	1897.	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
From Argentine Republic .	5,381	8,202	6,328	8,914	10,220	21,842	14,293	18,295	18,040	11,371	16,059
„ United States[1] . .	13,577	28,598	27,860	28,531	20,197	9,103	15,037	18,605	18,186	22,985	24,180
„ Australasia[2] . .	69,695	53,006	58,196	60,811	49,255	43,076	29,437	39,694	45,523	52,776	52,033
„ other countries. .	8,886	11,289	10,669	10,636	9,589	15,084	10,992	11,310	9,347	9,558	12,735
Total . .	97,549	101,096	103,057	108,900	89,261	88,105	69,759	87,904	91,096	96,690	105,007
Exports of Tallow . .	49,768	52,191	49,122	46,339	47,478	38,063	34,221	43,330	45,416	50,268	53,140

[1] These figures include "greases."

[2] Australasia includes New Zealand.

As a complement to the above table, I give in tabular form the shipments of Australian tallow to Europe :—

Australian Shipments to Europe

Year.	Tons.
1895	76,650
1896	48,250
1897	51,600
1898	45,000
1899	46,143
1900	47,000
1901	40,000
1902	32,400
1903	25,900
1904	35,400
1905	38,300
1906	43,100
1907	42,600

The amount of beef tallow exported from the United States in lbs., and its value in dollars, is given in the following table :—

Fiscal Year.	Lbs.	Dollars.
1896	52,759,212	2,323,674
1897	75,108,834	2,782,595
1898	81,744,809	3,141,653
1899	107,361,009	4,367,356
1900	89,030,943	4,398,204
1901	77,166,889	3,848,561
1902	34,065,758	1,924,577
1903	27,368,924	1,623,852
1904	76,924,174	3,801,302
1905	63,536,992	3,022,173
1906	97,567,156	4,791,025
1907	127,857,739	7,182,688

The imported tallows are chiefly of the first-named quality, viz. rendered tallow containing all the fat from the carcase. These tallows are sold according to their *titer* (*titre*) and *colour*. A description of the titer test has been given Vol. I. Chap. VIII., where also its commercial importance has been discussed, and titer test values of the commercial tallows have been tabulated.

As regards colour the commercial brands are differentiated as "good colour," "off colour," "no colour," etc., and are merely judged by the standards agreed upon between sellers and buyers on the London market. There is a further distinction made between "beef," "mutton," and "mixed" tallows.

During recent years, in consequence of the great demand for edible fats, the production of "premier jus" for export to Europe has been established on a large scale in oversea countries. Such tallow is not only carefully prepared from selected rough fat (see

above), but it is also filtered over fuller's earth, so that it arrives in a perfectly sound state in Europe, and when carefully packed will keep for months in a sound condition. Even the production of oleomargarine and oleostearine for export to Europe has assumed considerable dimensions during the last few years.

The exports of oleomargarine (oleo oil) from the United States during the last ten years in lbs., and its value in dollars, is given in the following table :—

Fiscal Year.	Lbs.	Dollars.
1896	103,276,756	8,087,905
1897	113,506,152	6,742,061
1898	132,579,277	7,904,413
1899	142,390,492	9,183,659
1900	146,739,681	10,503,856
1901	161,651,413	11,846,373
1902	138,546,088	12,254,969
1903	126,010,339	11,981,888
1904	165,183,839	12,873,558
1905	145,228,245	11,485,145
1906	209,658,075	17,445,976
1907	...	16,819,933

The dimensions which the trade in oleomargarine has assumed may be gathered from the following tables :—

Imports of Oleomargarine into the United Kingdom

Value.								
1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.
£ 257,595	£ 263,435	£ 300,253	£ 298,810	£ 292,988	£ 370,000	£ 324,115	£ 495,212	£ 591,058

Exports of Oleomargarine from the United Kingdom

	Value.								
	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.
	£	£	£	£	£	£	£	£	£
Exports of home production .	21,954	26,874	16,803	16,857	31,283	10,048	3,309	10,730	21,733
Re-exports of imports . .	56,410	53,076	87,834	83,438	60,566	81,082	80,347	188,731	205,363

On pressing tallow for the production of "stearine" tallow oil is obtained as a by-product.

Tallow oil (French—*Huile de suif*; German—*Talgöl*) is liquid or semi-solid according to the temperature at which it has been expressed. Tallow oil is chiefly used in admixture with mineral oils, as a lubricating oil. Its solidifying and melting points, as also its iodine values, naturally vary according to the conditions under which the tallow has been expressed. Hence the following characteristics have only limited application [1]:—

Specific Gravity at 100° C.	Titer Test. °C.	Iodine Value.	Iodine Value. Mixed Fatty Acids.	Maumené Test. °C.
0·794	34·5-37·5	55·8-56·7	54·6-57	35·0

BEEF TALLOW

French—*Suif de bœuf.* German—*Rindertalg.*
Italian—*Sego di bove.*

For tables of characteristics see p. 638.

Beef tallow when freshly rendered is nearly white, free from disagreeable odour, and almost tasteless. Such quality is represented by "Home-melt beef tallow." Imported tallow passes through all gradations, from "bleached" white to slightly yellowish tallow (Australian), through darker yellow (North American, South American) to finally the off-coloured lowest grades (North American, Australian "no colour").

Tallow was until recently considered to consist exclusively of the glycerides of palmitic, stearic, and oleic acids. The amount of olein used to be calculated from the iodine value. Thus a tallow absorbing 43 per cent of iodine was looked upon as containing 50 per cent of olein. It is not unlikely that owing to the influence of vegetable fats given with the food (oilcakes, etc.) less saturated acids than oleic acid may be found. *Farnsteiner* claims to have obtained small quantities of linolenic hexabromide, pointing to the presence of small quantities of linolenic acid in beef tallow.[2] Recent researches have further shown that it is no longer permissible to adopt the view that palmitin, stearin, and olein are contained as simple triglycerides in tallow, as the following mixed glycerides have been isolated by crystallising tallow from solvents:—oleodipalmitin, stearodipalmitin, oleopalmitostearin, palmitodistearin (see Vol. I. Chap. I.).

Recently *Bömer*[3] has shown that by frequently repeated crystal-

[1] Gill and Rowe, *Journ. Amer. Chem. Soc.* 1902, xxiv. 466.
[2] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1899, 25.
[3] *Ibid.* 1907, xiv. 196.

lisation of tallow from ether approximately $1\frac{1}{2}$ per cent of pure tristearin can be isolated.

The examination of tallow by the fractional distillation of the methylesters of its mixed fatty acids for the presence of small quantities of myristic acid is desirable (cp. "Lard," p. 614).

On treating beef fat, and oleomargarine, with 95 per cent alcohol in the same manner as described under "Lard" (p. 572), glycerides richer in olein pass into the alcoholic solution. The characteristics (1) of the original fat, (2) of the alcohol-soluble, (3) of the alcohol-insoluble portion are collated in the following table (*Arnold* [1]):—

[1] *Zeit. f. Unters. Nahr. u. Genussm.* 1907, 179.

[TABLE

	Butyro-refracto-meter at 40° C. "Degrees."	Saponi-fication Value.	Reichert-Meissl Value.	c.c. ½ KOH required for Insoluble Volatile Acids (Polenske's method).	Iodine Value.	Non-volatile Fatty Acids. Butyro-refracto-meter at 40° C. "Degrees."	Non-volatile Fatty Acids. Neutral-isation Value.	Non-volatile Fatty Acids. Iodine Value.	150 Grms. yielded Alcohol-soluble Portion. Grms.
Beef Fat									
I. Original Fat . . .	46·3	199·6	0·80	0·55	42·9	32·6	207·2	45·9	...
II. Alcohol-soluble Fat . .	47·2	196·0	0·88	0·70	54·0	36·7	203·7	55·9	6·8
III. Alcohol-insoluble Fat . .	46·4	200·5	0·61	0·60	42·1	32·0	207·8	43·9	...
Beef Fat									
I. Original Fat . . .	46·2	199·1	0·61	0·60	37·5	32·9	206·8	38·3	...
II. Alcohol-soluble Fat . .	50·2	193·9	0·94	0·80	55·5	38·1	203·0	57·5	5·0
III. Alcohol-insoluble Fat . .	46·0	200·5	0·55	0·55	36·2	32·4	207·9	37·4	...
Oleomargarine									
I. Original Fat . . .	47·4	199·4	0·66	0·55	46·3	33·2	208·3	48·1	...
II. Alcohol-soluble Fat . .	49·7	198·2	2·00	0·75	51·8	38·5	205·9	55·1	6·6
III. Alcohol-insoluble Fat . .	47·5	200·0	0·55	0·60	46·3	33·1	207·6	47·9	...
Oleomargarine									
I. Original Fat . . .	47·45	199·4	0·80	0·50	48·8	...	...	...	...
II. Alcohol-soluble Fat . .	48·6	193·6	1·30	0·75	54·4	...	...	...	...
III. Alcohol-insoluble Fat . .	47·3	199·8	0·70	0·55	48·5	...	...	...	...

The proportions of palmitin, stearin, and olein in the fats rendered from different parts of the same beast vary. *Mayer*[1] examined the fats obtained from different parts of the body of an Hungarian ox, three years old, with the results contained in the following table :—

[1] Wagner's *Jahresbericht*, 1880, 844.

Tallow from	Fat.			Fatty Acids.					
	Solidifying Point (Pohl's method).	Melting Point (Pohl's method).	Saponification Value.	Insoluble Acids + Unsaponifiable.	Solidifying Point (Pohl's method).	Melting Point (Pohl's method).	Neutralisation Value.	'Stearic Acid,'[1] Solidifying Point 54·8° C.	Oleic Acid, Solidifying Point 5·4° C.
	°C.	°C.			°C.	°C.		Per cent.	Per cent.
Intestines .	35·0	50·0	196·2	95·7	44·6	47·5	201·6	51·7	48·3
Lungs . .	38·0	49·3	196·4	95·4	44·4	47·3	204·1	51·1	48·9
Caul . .	34·5	49·6	193·0	95·8	43·8	47·1	203·0	49·0	51·0
Heart . .	36·0	49·5	196·2	96·0	43·4	46·4	200·3	47·5	52·5
Neck . .	31·0	47·1	196·8	95·9	40·4	43·9	203·6	38·2	61·8
Groins . .	35·0	42·5	198·3	95·4	38·6	41·1	199·6	33·4	66·8

[1] In the commercial sense of the term, *i.e.* mixed stearic and palmitic acids.

Physical and Chemical Characteristics of Beef Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.	Thermal Test. Heat of Bromination.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	°C.	Observer.	At 60° C.	Observer.
15	0·943-0·952	Dieterich	35-27 Temperature rises a few degrees without, however, remaining constant.	Rüdorff	45-46; 42-43, not below 40	Wolkenhaar	195·7-200	Filsinger	40	Hübl	0·25	6·1[3]	Archbutt	1·4510	Thoerner
50 (water 15·5=1)	0·8950	Allen			47·6-48·5	Dieterich	193·2-198	Köttstorfer	43·3-44	Wilson		6·7-7·2[4]	,,	Butyro-refractometer. "Degrees."	
98 (water 15·5=1)	0·8626	,,			43·5-45	Rüdorff		Deering	35·4-36·4	Filsinger					
100 (water 15=1)	0·860-0·861	Wolkenhaar						L. Mayer	35·6-38·9	Dieterich				At 40° C.	Observer.
100 (water 15=1)	0·860	Koenigs							45·2[1]	Wallenstein and Finck				49	Mansfeld
									38·3[2]	,,					
									38-40	Thoerner					
									41-47·5	Lewkowitsch					

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At 100° C. (water at 100=1)	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·6	Bensemann	0·8698	Archbutt	Titer Test.		43-44 and 46-47	Bensemann	197·2	Lewkowitsch	270-285	A. Wright	41·3	Williams	1·4375	Thoerner.
95·4-96	L. Mayer			43·5-45	Dalican	45	Hübl	201·6	Thoerner	284·5	Lewkowitsch	25·9-32·8	Morawski and Demski	Oleo-refractometer.	
				44·5	De Schepper and Geitel							Iodine Value of the Liquid Fatty Acids.		"Degrees."	Observer.
				43 Cp. Chap. VIII.	Hübl Lewkowitsch							92·4[1]	Wallenstein and Finck	−40	Jean
												92·2[2]	,,		

[1] Australian. [2] Berlin town tallow. [3] American beef. [4] Home-refined.

On the assumption that the fatty acids of tallow consist of palmitic, stearic, and oleic acids only, an assumption which may be considered as correct for all practical purposes, the composition of a sample may be arrived at by determining the proportion of stearic acid in a direct manner by the method described Vol. I. Chap. VIII. In the examination of several samples of tallow the author found from 21 to 22 per cent of stearic acid. The specimen examined by *Kreis* and *Hafner* (see table, p. 608), of the iodine value 35·8, gave 39·5 per cent of stearic acid.[1] The proportion of oleic acid can be calculated from the iodine value; the difference gives then the amount of palmitic acid. The variations in the percentage of stearic acid in beef fat from different parts of the body of the same animal are implicitly expressed by the percentages of "stearic acid" of solidifying point 54·8° C. given in the table, p. 637. (It should, of course, be noted that the "stearic acid" includes palmitic acid.)

It has been pointed out already that tallow frequently undergoes a "demargarinating process," by being subjected to pressure in hydraulic presses, when "beef stearine" and "tallow oil" are obtained (see p. 634).

Beef stearine varies in its chemical composition, not only owing to the variation of different specimens of tallow, but also with the pressure applied in the hydraulic press and with the length of time during which the pressure has been allowed to act on the tallow. Commercial samples of beef stearine have melting points varying, as a rule, from 49° to 53° C. The iodine value varies from 8 to 15 and even to 20, and the percentage of stearic acid rises in inverse ratio to the decrease of the iodine value; thus *Hehner* and *Mitchell* found in a beef stearine absorbing 2·0 per cent of iodine 50·2 to 51·1 per cent of stearic acid. Recently *Bömer*[2] has shown that by frequently repeated crystallisation of beef stearine from ether approximately 4·5 per cent of pure tristearin can be isolated. It should be noted that beef stearine is more soluble in petroleum ether (of specific gravity 0·648) and methylated ether (of specific gravity 0·7175) than is lard stearine (*Dunlop*). This is of importance in the detection of beef stearine in lard (cp. "Lard," table, p. 612).

Beef stearine obtained from "premier jus" is used for edible purposes in the manufacture of margarine, as also in the manufacture of compound lards and in the preparation of "suet substitutes" (see Vol. III. Chap. XV.).

The amount of free fatty acids in tallow varies considerably with the state of purity. In freshly rendered tallows the proportion of free fatty acids is negligible and rarely exceeds 0·5 per cent; in commercial samples the percentage of free fatty acids may rise to 25 per cent and even more. Hence the acetyl values shown by

[1] It should, however, be noted that *Kreis* and *Hafner* did not determine the melting point of their "stearic acid," hence the figure 39·5 per cent must be accepted with reserve.

[2] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1907, xiv. 111.

tallows of different states of purity will also vary. Thus *Lewkowitsch* found acetyl values varying from 2·7 to 8·6 in different brands of tallow. It need hardly be repeated (cp. Vol. I. Chap. VI.) that these acetyl values do not indicate the presence of hydroxylated acids. In this connection it may be pointed out that *Fahrion*[1] found in a specimen of tallow 0·13 per cent of "oxidised" acids.

The valuation of "*premier jus*" and oleomargarine is based in the first instance on the taste and on the absence of free fatty acids and freedom from rancidity. Samples of oleomargarine examined by the author contained from 0·29 to 0·6 per cent of free fatty acids. Notwithstanding this amount of free fatty acids, these oleomargarines were perfectly suitable for the manufacture of margarine and other preparations intended for edible purposes. The determination of the iodine value and of the melting point is of secondary importance and need only be resorted to if special circumstances demand examination in this direction. With regard to the detection of colouring matters in edible tallow cp. p. 660, and Vol. III. p. 18.

The valuation of commercial tallow for the purposes of the soap- and candle-maker is based, in the first instance, apart from the colour, on the *proportion of water and non-fatty acids* and on the solidifying point ("titer") of its fatty acids.

The proportion of water is determined in the usual manner. The following commercial method was introduced by *H. Norman Tate*:—Heat 50 grms. of the sample in a porcelain crucible or a silver crucible to 130° C. and keep it thereat until bubbles cease to be given off and the melted fat is in a condition of calm fusion without giving off vapours. The fat is then allowed to cool, and is weighed. The loss is calculated as moisture (cp. Vol. I. Chap. IV., also p. 623). In the case of pure fats *Tate's* method yields correct results. Owing, however, to the property of lime soaps (sometimes fraudulently admixed with tallow) to retain moisture the results are too low. This happens especially in the case of bone fats (cp. p. 623), as is shown by the following analyses, due to *Shukoff* and *Schestakoff*:—

Moisture in Bone Fats

Usual Method. Per cent.	Norman Tate's Method. Per cent.
2·80	1·90
6·11	4·30

Impurities—not fat—are determined as described, Vol. I. Chap. IV. (cp. also bone fat, p. 623). The titer test must be determined with due observance of the details given in Vol. I. Chap. VIII.

The higher the titer the more valuable is the tallow for the purposes of the candle-maker and soap-maker. The following empirical table compiled by *Dalican* is still used in a number of candle-works for an approximate estimation of the yield of commercial

[1] *Zeit. f. angew. Chem.* 1898, 784.

stearic acid from tallows having the solidifying points recorded in the first column of the table :—

Solidifying Point. Titer Test.	Commercial Stearic Acid.	Oleic Acid.
° C.	Per cent.	Per cent.
35	25·20	69·80
35·5	26·40	68·60
36	27·30	67·70
36·5	28·75	66·25
37	29·80	65·20
37·5	30·60	64·40
38	31·25	63·75
38·5	32·15	62·85
39	33·44	61·55
39·5	34·30	60·80
40	35·15	59·85
40·5	36·10	58·90
41	38·00	57·00
41·5	38·95	56·05
42	39·90	55·10
42·5	42·75	52·27
43	43·70	51·30
43·5	44·65	50·35
44	47·50	47·50
44·5	49·40	45·60
45	51·30	43·70
45·5	52·25	42·75
46	53·20	41·80
46·5	55·10	39·90
47	57·95	37·05
47·5	58·90	36·10
48	61·75	33·25
48·5	66·50	28·50
49	71·25	23·75
49·5	72·20	22·80
50	75·05	19·95
50·5	77·10	17·90
51	79·50	15·50
51·5	81·90	13·10
52	84·00	11·00
52·5	88·30	6·70
53	92·10	2·90

Tallows of a lower titer than 44° C. are unprofitable to the candle-maker, and are therefore chiefly employed for soap-making.

A large amount of **free fatty acids** depreciates the value of a tallow considerably, as the candle material obtained from such tallow in the lime saponification process turns out dark; also soap made from such tallow has an inferior ("foxy") colour.

In the valuation of tallow for *lubricating purposes* the titer test is of secondary importance, whereas the determination of the amount of free fatty acids affords the necessary guidance.

Adulterants in tallow are easily detected by means of the quantitative reactions.[1] If required, the phytosteryl acetate test

[1] The different behaviour of cocoa nut oil and palm kernel oil soaps from that of tallow soap to solutions of common salt and caustic alkalis has been frequently

may be applied for the detection of vegetable oils and fats. It must, however, be added that at present tallow is but rarely adulterated with vegetable oils or fats. A not infrequently used adulterant is "whale stearine." Home tallow is sometimes adulterated with *distilled grease stearine*. This "stearine" is obtained by distilling "recovered grease," and expressing the liquid portion from it; it consists chiefly (Chap. XVI.) of stearic acid, iso-oleic acid, and small quantities of cholesterol and isocholesterol.[1] A tallow thus adulterated has a peculiar smell, a high acid value, and a somewhat high amount of unsaponifiable matter. If the latter be boiled with acetic anhydride a green fluorescence,[2] after adding conc. sulphuric acid, would point to the presence of isocholesterol and, inferentially, of distilled grease stearine. The fatty acids obtained from tallow thus adulterated turn yellow after a few days, and exhibit the peculiar smell characteristic of wool fat and its derivatives.

A high acid value may point to admixed stearic acid ("cotton stearine") from cotton seed mucilage (Chap. XVI.); in that case, of course, the isocholesterol reaction will not be obtained, but the acid value and the amount of unsaponifiable matter will be found high.[3]

Goat's tallow, sold in commerce as mutton tallow, is considered by candle-makers as an adulterant. Although such tallow has a high melting point, it is not suitable for candles owing to its fatty acids not crystallising readily, but solidifying to an amorphous mass, from which it is difficult to remove the imprisoned oleic acid. The candles prepared in the ordinary way from goat's tallow are of low quality, do not possess the metallic ring of first-class candles, and easily become discoloured through their persistently retaining oleic acid. Goat's tallow is best detected by the smell given off on warming the sample (*Chevreul's* "acide hircique").

This class of tallow plays an unimportant part in the world's market.

MUTTON TALLOW

French—*Suif de mouton.* German—*Hammeltalg.*
Italian—*Sego di montone.*

For tables of characteristics see pp. 644, 645.

Mutton tallow closely resembles beef tallow; it is frequently mixed with the latter and is then sold as "mixed tallow." Mutton

employed as a means of detecting cocoa nut and palm nut oils in tallow. Such methods have been detailed in the second edition of this work, pp. 596-597, but were omitted in the third edition, having been superseded by more expeditious methods. They are referred to here because the same principle has again been proposed recently (Cohn, *Chem. Zeit.* 1907, 854).

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 142. [2] *Ibid.* 1892, 144.

[3] In Germany paraffin oil is used by the custom-house officers for "denaturing" tallow if caustic soda be objected to. According to the regulations of the United States Department of Agriculture tallow which is unfit for edible purposes must be denatured either with sufficient kerosine (burning oil), or with coal-tar creosote, to give it a distinct taste of these substances, or with the colouring matter "Sudan III."

tallow is, as a rule, harder than beef tallow, and consequently its solidifying and melting points, as also those of its fatty acids, are higher; it is more liable to turn rancid than is beef tallow. For this reason it cannot be used in the manufacture of first-class butter-substitutes or high-class toilet soaps.

Recently *Bömer*[1] has shown that by frequently repeated crystallisation of mutton tallow from ether approximately 3 per cent of pure tristearin can be isolated.

Mutton "stearine" behaves with solvents (petroleum ether and ordinary ether) much like beef stearine (cp. tables under "Lard").

The fat rendered from different parts of two sheep gave, according to *Moser*,[2] the following results:—

Fat from	Fat.			Fatty Acids.	
	Solidifying Point.	Melting Point.	Saponification Value.	Solidifying Point.	Melting Point.
	°C.	°C.		°C.	°C.
Kidneys . . .	40·7-40·9	51·0-55·0	194·8-195·2	51·9-51·9	56·2-56·5
Caul and intestines .	39·2-39·7	52·0-52·9	194·6-194·8	50·4-50·6	54·9-55·8
Adipose tissue .	34·1-34·9	49·5-49·6	194·2-194·4	43·7-46·2	50·7-51·1

A specimen of mutton tallow of the iodine value 42·5 contained 35·5 per cent of stearic acid[3] (*Kreis* and *Hafner*).

The information contained in the following table, due to *Hehner* and *Mitchell*,[4] is very instructive; the different specimens of fat were taken from a Scotch sheep eighteen months old:—

Fat from	Iodine Value.	Melting Point of Fatty Acids.	Stearic Acid.
	Per cent.	°C.	Per cent.
Kidneys . .	48·16	45·6	26·2-27·7
Back . .	61·3	41·4	24·8
Neck . .	48·6	42·2	16·4
Breast . .	58·2	33·8	About 1
Ham . .	50·6	40·8	No deposit after two days.

A special kind of mutton tallow is "graisse de couyrouck," obtained from the extraordinarily developed caudal appendix of a Turkish sheep.

[1] *Zeit. f. Unters. d. Nahrgs. u. Genussm.* 1907, xiv.

[2] *Bericht der Thätigkeit der Landw. Versuchsstation, Wien*, 1882, 1883.

[3] It should, however, be noted that *Kreis* and *Hafner* did not determine the melting point of their "stearic acid," hence the figure 35·5 per cent must be accepted with reserve.

[4] *Analyst*, 1896, 327.

Physical and Chemical Characteristics of Mutton Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·937-0·953	Dieterich	36-32 (rising several degrees)	Rüdorf	47-49	Dieterich	192-195·2	Thoerner
100	0·860	Koenigs			46·5-47·4	Rüdorf		
,,	0·858	Thoerner	40-41	Thoerner	44-45	Thoerner		

Physical and Chemical Characteristics of Mutton Tallow—continued

Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
35·2-46·2	Wilson	8·1 [1]	Hehner and Mitchell	1·4501	Thoerner
34·8-37·7	Dieterich				
32·7	Thoerner	7·6 [2]	,, ,,		
43-44	,,	7·55 [3]	Archbutt		
38·6	Wallenstein and Finck	8·9 [4]	,,		

[1] From kidney. [2] From flare. [3] Australian mutton. [4] Home-refined.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·54	Bensemann	41 39	Thoerner ,,	49-50 and 53-54 49 46-47	Bensemann Thoerner ,,	210	Thoerner	34·8	Thoerner	1·4374	Thoerner
		Titer Test.						Iodine Value of the Liquid Fatty Acids.			
		45-46 also 43·2 46·1 See Chap. VIII.	Dalican de Schepper and Geitel Lewkowitsch					92·7	Wallenstein and Finck		

BUTTER FAT

French—*Beurre de vache.* German—*Butterfett.*
Italian—*Burro di vacca.*

Butter fat or milk fat is contained in cow's milk.

The production of butter on the farm is one of the oldest house industries, and is so well known that it requires no description here. Moreover, as a house industry it is rapidly dying out in the densely populated countries, not only on account of the naturally limited amount of milk that can be provided for this purpose in any one locality, but also because the essential conditions for butter production, viz. cleanliness and cooling arrangements, cannot be attained readily. The house industry is rapidly giving way in all butter-producing countries to a large scale manufacture in *creameries*, *i.e.* establishments which collect the fresh milk from a number of farms and work it up into butter. These creameries may well be likened to a factory dealing with the production of edible oils and fats. In these factories the chief essentials on which successful manufacture rests can be scrupulously observed. The milk is received in the freshest state possible, pasteurised if necessary, and the cream separated by *milk separators*,[1] which are either worked by hand or are belt-driven. The best known belt-driven machines are the Alpha-Laval cream separators, which furnish in the form of cream the largest amount of the fat contained in the milk. The ripening of the cream (either by naturally prepared "*starters*" or by "*pure culture starters*") is also carried out in these establishments with scrupulous cleanliness, which is hardly practicable in a farm-house. The churning[2] of the ripened cream is practically a mechanical process and consists in causing the butter fat globules to coalesce and so to form the commercial butter; it is carried out in these establishments on a manufacturing scale, as is also the washing and the "working" of the butter on the "butter table." The object of these latter operations is to remove as far as possible the milk which is detrimental to the keeping of the butter. On the butter table, if required, salt also is added. The machinery employed throughout is similar to that described under "Margarine Manufacture," Chap. XV. In fact, it may be said that the greatest impetus has been given to the production of butter on a manufacturing scale through the margarine manufacture.

Butter produced in these establishments is known as "creamery butter."

In consequence of the insufficiency of the European home production, enormous amounts of butter are imported into Europe. A

[1] For a Canadian "butter separator," cp. *Canada, Department of Agriculture, Central Experimental Farm, Ottawa, Ont., 1906*, Ottawa, 1907.

[2] E. V. Schou (English patent 5810, 1908) dispenses with churning by passing ripened cream over chilled rollers. Cp. also A. H. Borgström, French patent 387,653 (1908).

large quantity of such butter is sold in its original form. By no means insignificant amounts are, however, "blended" in "butter factories" with home-produced butter on butter tables (see Fig. 1, Vol. III.) or in mixing machines. The mixture is still, of course, butter; but it can be differentiated from "creamery" butter by its different "grain" or "texture," the natural smooth grain of the once finished butter having been "broken" by the mixing together, on the butter table, of the foreign butter with butter produced in creameries.

Such butter is known as "factory butter."[1]

With the increased production of butter the difference between "creamery butter" and "factory butter" tends to disappear more and more. Some of the largest creameries can now hardly be differentiated from factories, the creamery butter produced by them being only a small fraction of their total output of butter. Even creameries have, therefore, commenced to add to their butter boric acid as a preservative, so that one characteristic difference that once distinguished creamery butter from factory butter has practically ceased to exist. Indeed, creameries no longer guarantee the whole of their output as free from boric acid, a warranty in that respect being only given for limited amounts sold at a higher price.

Even in oversea countries the necessity has arisen for collecting the produce of a number of farms and blending it in central establishments. In New Zealand these establishments are termed "packing-houses," and the butter prepared there is shipped as "milled butter," this word having been chosen to distinguish this butter from creamery and factory butters.

The chief butter-exporting countries of Europe are Denmark, Russia, Holland, France, and Sweden.

Home Production, Exports and Imports, of Butter of several European Countries

Country.	Home Production (estimated).	Exports.		Imports.	
		1902.	1904.	1902.	1904.
	Tons.	Tons.	Tons.	Tons.	Tons.
Denmark .	...	69,770	81,530	7000	5900
Russia . .	...	37,821	39,492	245	360
Holland .	60,000	22,861	23,607	680	2654
France[2] .	130,000	24,041	22,628	5462	4567
Sweden .	...	20,054	19,570	521	592

[1] According to another definition, "factory butter" is made by the old process of putting milk in dishes and allowing the cream to rise before separating, whereas "creamery butter" is obtained from milk by the aid of centrifugal apparatus.

[2] Fuller details will be found in Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires, traduit par E. Bontoux*, p. 1262.

Smaller quantities of butter are exported from Finland,[1] Norway, Italy, and Belgium. Germany has practically ceased to be a butter-exporting country, and she now imports considerable quantities from Denmark, Holland, Sweden, Finland, Siberia, and oversea countries.

The imports into Germany were, in 1902, 16,689 tons (exports 2199), and had grown in 1904 to 34,399 tons (exports 801), whilst the total home production amounted to about 120,000 tons. Switzerland is now a butter-importing country.

The amount of butter produced in the United Kingdom in the three years 1903 to 1905 averaged 163,140 tons, while the average annual imports less exports were 203,301 tons. The average quantity consumed per head of population, calculated from these figures, was as follows :—

Home-produced butter . . .	8·5 lbs.
Imported butter	10·7 lbs.
Total	19·2 lbs.

Large quantities of butter are now imported into Europe from Australia, Canada, the Argentine, New Zealand, and Siberia.

The importance which the butter trade has acquired in the world's market may be best illustrated by the following table which deals with the United Kingdom, the chief butter-importing country of Europe :—

[1] The importance which Finland has gained as a butter-exporting country may be gathered from the following table :—

Exports of Butter from Hangö, Finland

	1904. Cwts.	1905. Cwts.	1906. Cwts.
To Great Britain	183,392	224,540	232,516
,, Denmark	42,795	56,705	38,845
,, other countries	5,992	22,800	15,547
	232,179	304,045	286,908

[TABLE

Imports of Butter to the United Kingdom

	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
Quantities in cwts.	...	2,372,603	3,351,752	3,692,335	3,966,876	4,027,766	4,254,185	4,157,778	4,344,346	4,210,156
Value in £ . . .	15,961,783	17,213,516	17,450,435	19,297,396	20,526,690	20,798,707	21,117,162	21,586,662	23,460,196	22,417,926

Exports of Butter from the United Kingdom

	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
Quantities in cwts.	...	...	...	...	...	12,191	9,566	9,062	12,966	12,305
Value in £ . . .	59,731	53,195	55,792	59,376	79,130	63,341	51,354	49,155	68,457	68,591

Re-exports of Butter from the United Kingdom

	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
Quantities in cwts.	...	...	...	...	...	63,511	86,666	70,518	77,504	83,591
Value in £ . . .	319,806	257,999	258,934	254,746	227,576	312,703	409,319	357,658	396,995	418,643

In order to show which countries are chiefly supplying the United Kingdom with butter, I append the following table :—

Imports of Butter into the United Kingdom

Countries from which imported.[1]	Quantity. Cwts. 1906.		Quantity. Cwts. 1907.	
Foreign Countries :—				
Argentina	48,737		51,122	
Belgium	42,239		22,120	
Denmark	1,675,761		1,818,811	
France	319,401		281,306	
Germany	10,701		7,297	
Iceland and Greenland	2,319		2,804	
Netherlands	195,366		168,496	
Norway	29,302		23,465	
Russia	606,549		657,649	
Sweden	182,803		226,740	
Tripoli	23		...	
Turkey	5		...	
United States of America	157,312		1,063	
Uruguay	160		...	
Foreign Countries—Total		3,270,678		3,261,115
British Possessions :—				
New South Wales	180,655		195,289	
Victoria	287,190		288,670	
Queensland	77,982		97,685	
South Australia	15,287		17,342	
Australia—Total[2]	561,114		598,986	
Canada	190,968		34,753	
Cape of Good Hope	977		...	
Channel Islands	1		...	
Indies, East, British	1,848		1,439	
New Zealand	311,672		313,863	
British Possessions—Total		1,066,580		949,041
Total		4,337,258		4,210,156

Further statistical data regarding New Zealand and Siberia will be found below.

The examination of butter divides itself naturally into two parts : (1) The examination of the whole butter ; (2) The examination of the butter fat.

[1] The countries named above are those from which the quantities shown were received and are not necessarily the countries of origin.

[2] The total amount of butter produced in Australia during the years 1902-6 was as follows :—

Year.	Lbs.
1902	79,572,327
1903	100,332,242
1904	140,255,208
1905	140,898,726
1906	159,870,662

Under the first heading I shall consider the examination of butter on the assumption that the fat contained in it is genuine milk fat.

(1) Examination of Butter

Butter must be looked upon as an emulsion of fat and water containing small quantities of "casein" ("curd"), milk sugar, and inorganic salts. In those butters which are salted in the last stage of the manufacturing operation common salt will also be found. The following table, due to *Vieth*, gives a number of analyses of butter:—

Origin of Butter.	Fat.	Curd.	Salt.	Water.
	Per cent.	Per cent.	Per cent.	Per cent.
English . .	86·85	0·59	1·02	11·54
French . .	84·77	1·38	0·09	13·76
,, salted .	84·34	1·60	2·01	12·05
German . .	85·24	1·17	1·35	12·24
Danish . .	83·41	1·30	1·87	13·42
Swedish . .	83·89	1·33	2·03	13·75

The percentages of fat given in the last table vary within somewhat narrow limits, as the percentages of water do not differ widely. Butters containing as much as 90 per cent of fat are rarely met with. The percentage of fat in commercial butters rather tends to fall to the neighbourhood of 80 per cent, inasmuch as the maximum percentage of water which butter may contain has been legally fixed in many countries at 16 per cent. Naturally the tendency is, especially in butter factories, to regulate the composition of the product so that it may contain as high a percentage of water as the particular circumstances—nature of raw material, time of the year, etc.—permit.

With regard to butter having exceptional percentages of water see p. 653.

The examination of butter comprises the determination of **water, solids-not-fat,** and the detection of **colouring matters** and **preservatives.** Gross adulterants, such as *starch, potato pulp, ground white cheese,* etc., will hardly occur at present, since the sophistication of butter has assumed a more scientific character, and is practically confined to the addition of foreign fats. The adulteration with foreign fats will be considered under "(2) Examination of the Butter Fat" (p. 667).

1. **Water** is determined by drying a properly drawn average sample (cp. Chap. IV.) at 100° C. The Society of Bavarian Analytical Chemists recommend drying the butter at 100° C. for six hours, with occasional stirring. This would appear far too long a time for so simple a determination. Moreover, this *modus operandi* is liable to lead

to errors, as, on the one hand, loss may occur through volatilisation of any free fatty acids, and on the other hand, an increase of weight may take place through their oxidation. The method of *Henzold*, described Vol. I. Chap. IV., has, therefore, come more into vogue, especially in Germany, but even in this method the heating for two hours appears to be somewhat long. No doubt every analyst will be able to settle so simple a question by his own experience.[1]

In cases where scientific accuracy is not the chief object, as for market control, the amount of water may be determined rapidly by *Birnbaum's* method as modified by *Wibel*[2] in the following manner: 10 grms. of butter are shaken up with 30 c.c. of ether, previously saturated with water, in a tube corked at one end and provided with a stop-cock at the other, through which the separated aqueous liquid is run off into a second narrow graduated tube, containing 5 c.c. of saturated brine and a trace of acetic acid, so as to give a distinct red colour with litmus. The increase of volume, due to the water in the butter, is then read off. The results are stated to be but slightly below those obtained by gravimetric analysis.[3]

Many other rapid methods and apparatus have been proposed. Their description necessarily falls outside the scope of this work, as they are unable—and indeed do not pretend—to furnish accurate quantitative results.

The proportion of water in butter depends to a large extent on the skill of the producer, shown by observing the proper temperature and regulating the final stages of the "working" of the butter so as to eliminate as much water as possible. As the knowledge of proper modes of manufacturing is being spread through dairy schools, and suitable appliances for expressing the excess of water are being introduced largely, the proportion of water in European butters lies now mostly between 11 and 14 per cent, although it may rise to 16 per cent.

If butter is made at a somewhat high temperature—as is the case in the west of Ireland—the water cannot be removed so readily as in dairies in which the cream is cooled properly; the proportion of water in "Irish butter" is therefore high, rising to 25 per cent and more.

In this country the limit of 16 per cent for the proportion of water in butter has been legalised, and such exceptional butter as Irish butter may only be sold provided a sufficient disclosure is made to the purchaser.

Some butters imported from abroad have a low percentage of water (see below) and are, therefore, dry and hard owing to their having been kept in cold storage, and difficult to handle in the retail

[1] For *Crismer's* method of determining the amount of water by means of the critical temperature of dissolution the reader must be referred to the *Bullet. de l'Assoc. Belge des Chim.* 1896 (9), 359; *Analyst*, 1896, 241. Cp. A. Schoonjan's *Bull. Soc. Chim. Belg.* 1908, 342.

[2] *Journ. Soc. Chem. Ind.* 1893, 630.

[3] Cp. also Poda, *Zeit. f. Unters. Nahr. u. Genussm.* 1901, 492; F. Bengen, *ibid.* 1908, xv. 587; G. R. Geldard, English patent 18,496, 1902; M. Vogtherr, French patent 324,745, 1902; Nicholl's "Sensible-Apparatus," *Chem. Zeit.* 1908, 1140.

trade. In consequence of this difficulty there has sprung up a trade, the object of which is to incorporate water with such butters. Under the pretence of making such butters—chiefly colonial butters—more easy to handle in the retail trade, there is now being sold under the name of **milk-blended butter** an artificially prepared butter, containing from 20-25 per cent of water. It is manufactured by mixing skimmed milk or whole cream with butter, and adding preservatives so as to prevent the milk from "souring." It is evident that this is tantamount to incorporating water with butter. At first this adulterated butter was sold as "butter," but owing to the interference of the law the name was changed into "milk-blended butter."[1]

According to the "Butter and Margarine Act" of 1907 the sale of milk-blended butter is permitted provided this butter contains no more than 24 per cent of water. I append a few analyses of "milk-blended" butters :—

Analysis of Milk-blended Butters[2]

	Per cent.	Per cent.	Per cent.
Water . . .	25·1	22·6	21·1
Fat . . .	65·2	73·0	73·1
Casein . . .	7·0	2·8	2·7
Salt, etc. . . .	2·7	1·6	3·1
	100	100	100
Reichert-Meissl value of fat . .	34·4	31·3	

In the following tables I give a number of analyses stating the percentages of water in commercial butters. The numbers of the following table (*Vieth* and *H. D. Richmond*[3]) are arranged by the author according to the percentages of water :—

Kind of Butter.	Number of Samples examined.	Samples containing per cent of Water.			Observer.
		From 11-14.	From 10-15.	Above 16.	
		Per cent.	Per cent.	Per cent.	
English and foreign .	560	83·8	94·2	0·9	Vieth
English . .	143	70·7	85·4	0·7	H. D. Richmond
Foreign . .	417	88·3	97·2	1·0	,,
French . .	451	...	...	8·6	,,
,, . .	48	...	...	0·0	,,

[1] Although this mixture of milk and butter had been the subject of numerous prosecutions under the Sale of Food and Drugs Acts, no High Court decision had been given in this matter, so that it was held that the seller of milk-blended butter was protected provided that a sufficient disclosure had been made to the purchaser at the time of sale.

[2] F. Clowes, *Report from the Select Committee on Butter Trade*, 1906.

[3] *Analyst*, 1894, 17.

In the following table *Martiny's*[1] numbers, referring to more than 20,000 separate analyses, are collated :—

Country.	Water. Per cent.	Number of Samples.
England . .	11·18	334
Germany—		
Fresh butter .	13·96	523
Salt butter .	13·01	1107
France . .	13·40	225
Denmark . .	13·99	9847
Sweden . .	13·66	4423
Finland . .	11·18	438

The percentages of water in imported butters (into England) are summarised in the following table (figures exceeding the permissible maximum of 16 per cent have been omitted from the first horizontal line) :—

Origin.	Percentage.
Argentine, French, Italian . . .	12-16
Danish	14-16
Canadian	12-16
Australian	12-15
New Zealand	9-15
Siberian	9-14

For purposes of "butter-blending" New Zealand and Siberian butters have assumed considerable importance. No doubt the fact that the law permits up to 16 per cent of water may induce the "butter-blenders" to add in "blending" so much water as to come as near as possible to the allowed limit. Undoubtedly some admixture of water is made,[2] and will be continued as long as the cost caused by the proper controlling of the percentage of water in the final product does not militate against this practice; but the extent to which this practice takes place seems to be magnified to an enormous degree in the imagination of those who are not acquainted with the conditions underlying manufacturing processes. Since butter-blending is considered in the eyes of the law a legitimate industry, it is impossible to trace the addition (if any) of water made in the "blending process."

In order to show what quantities of butters low in contents of water are available, I give the following statistical data referring to New Zealand butter :—

[1] *Landw. Jahrb.* 1898, 773. [2] Cp. *Revue intern. des falsific.* 1907 (20) 97.

[TABLE

Export of Butter from New Zealand

Year.	Tons.	Value.
1886	1,159	£105,537
1887	850	54,921
1888	1,499	118,252
1889	1,898	146,840
1890	1,741	122,701
1891	1,972	150,258
1892	2,697	227,162
1893	2,907	254,645
1894	3,039	251,280
1895	2,898	227,601
1896	3,567	281,716
1897	4,950	402,605
1898	4,840	403,690
1899	6,804	571,799
1900	8,629	740,620
1901	10,080	882,406
1902	12,699	1,205,802
1903	14,255	1,318,067
1904	15,718	1,380,460
1905	17,143	1,514,156
...	...	...
1907	...	1,615,622

The first creameries in *Siberia* were opened in 1893, and since then their number has increased to a great extent. The export of butter from Siberia to Europe has risen from 5,416,800 lbs. in 1899 to 90,280,000 lbs. in 1902. (Even this did not represent the total export from Siberia, as considerable quantities had been sent to China and Japan. With the improved conditions of transport and the introduction of proper methods of dairying, even in the villages of the Altai mountains, the Siberian export will rise rapidly.)

2. **Solids-not-fat** are best determined in the sample of butter previously employed for the estimation of water, by exhausting the dried butter with ether, chloroform, carbon bisulphide, or petroleum ether, and weighing the residue after drying.

If a fresh quantity of butter be taken for this determination, due attention must be paid to the fact that butter is not a homogeneous product, as different parts of the sample contain varying amounts of butter-milk.

The solids-not-fat consist of *casein*, *milk-sugar*, and *inorganic salts*. By exhausting the dried residue with water, to which a trace of acetic acid has been added, milk-sugar and the bulk of the inorganic salts are removed, leaving casein behind; its weight is ascertained after drying. The minute quantity of salts retained in the casein and found on incineration is then deducted. *Koenig* suggested to determine the proportion of nitrogen by *Kjeldahl's* process and multiply the result by 6·25. Both methods yield identical results. The proportion of casein (curd) in butter varies according to the length of time the milk (or the cream) has been allowed to stand previous to

churning. The percentages found vary, as a rule, between 0·5 and 2·25 per cent. The figure 4·78 recorded by *Koenig* must be considered an exceptional one.

The amount of casein (curd) has latterly become of some importance, as adulteration of butter has been carried out by means of curd obtained from milk (either by coagulating it with the help of rennet or by adding a little dilute hydrochloric acid, pressing the separated curd and converting it, with the assistance of sodium carbonate, into a jelly). The addition of such curd permits at the same time an increased amount of water to be held by the butter without its becoming readily noticeable, unless recourse be had to chemical analysis. Any butter containing more than 2 per cent of curd should be looked upon with suspicion.

The following is the analysis of an adulterant of this kind[1]:—

	Per cent.
Water	65·46
Fat	0·08
Sugar	2·24
Soluble proteids	0·69
Ash of soluble portion	0·35
Ash of insoluble portion	0·67
Casein by difference	30·5

A genuine butter containing 0·23 per cent of casein and 11·51 per cent of water showed, after admixture of 5 per cent commercial casein, 0·90 per cent of curd and 16·02 per cent of water.

The amount of *inorganic salts*, chiefly sodium chloride, is found by igniting the ether-insoluble residue from 10 grms. of butter, taking care, however, not to heat the ash to too high a temperature lest sodium chloride should volatilise. The proportion of sodium chloride is ascertained by titration with standard silver solution, using potassium chromate as an indicator. Sodium chloride is determined with greater accuracy by melting in a porcelain dish 10 grms. of butter with an equal amount of paraffin wax and 50 c.c. of water, previously acidulated with a few drops of nitric acid, and stirring the melted mass. After cooling, the cake is taken off and rinsed carefully, the aqueous liquid is then filtered, and silver nitrate is added.

The proportion of sodium chloride in 113 samples examined by *J. Bell* was found lying between 0·4 and 9·20, the majority of the samples yielding from 2 to 7 per cent; only in one case 15·08 per cent was found. The amount of salt added to butter varies, of course, in different countries and localities. An excessive amount of ash will naturally invite further examination.

Milk-sugar is not determined direct, but found by difference.

Fraudulently added substances of a non-fatty nature, such as *starch*, *borax*, etc., are detected as described Vol. I. Chap. IV.

The proportion of **butter fat** is likewise found by difference; it

[1] *Analyst*, 1906, 177.

can, of course, be determined direct by evaporating the ether-extract and weighing the residue.[1]

3. **Preservatives.**—Well made butter from which the butter-milk has been expressed carefully, and which has been washed properly, will remain "sweet" for a sufficient length of time. In the manufacture of "*milk-blended*" butter the admixture of preservatives is a necessity, as the presence of milk—like that of all organic putrescible substances—tends to increase the liability of butter to become rancid, and at last unfit for consumption. In the case of carefully prepared home-produced butter the addition of preservatives, except perhaps pure salt, is unnecessary.

A harmless preservative of butter is *salt*, and butter so preserved will keep for several weeks, and in cold storage even for months. Such butter is known in the trade as salt butter, to differentiate it from fresh butter, which is practically free from added salt. The latter butter is either sold in the fresh state, or preserved, by being kept (shipped) in cold storage. (See Appendix.)

Saltpetre is perhaps not so harmless as common salt. This preservative has not yet been the subject of extensive physiological experiments, although it seems to be used frequently in butters imported from oversea countries.[2]

Other preservatives are, however, frequently used to prevent rapid deterioration of butter which is made in a careless or uncleanly manner. Notwithstanding the fact that butter made in home dairies should not require the addition of any preservative, yet at certain seasons 0·25 per cent of boric acid is added even in well-conducted creameries. Colonial butter is usually preserved by the addition of a mixture of borax and boric acid, amounting in terms of boric acid to about 0·5 per cent, a quantity which has been approved of, as it were, by the Preservatives Committee (in England). In Italy the addition of 0·2 per cent of borax is permitted. In the Argentine the admixture of boric preservatives is forbidden.

With the importation of butter from foreign countries the necessity of preserving it has become imperative, and salt has been replaced by other preservatives, some of which are considered innocuous, whereas others must be looked upon as dangerous to health and are, therefore, forbidden.

Amongst the first class of preservatives are included boric acid, borax, boroglycerin, glucose; amongst the second class formalin, benzoic acid and benzoates, and fluorides. Salicylic acid should be considered as standing midway between the two groups. Hence there arises the necessity for examining butter for the presence of these preservatives.

Borax will be detected on examining the ether-insoluble portion.

Boric acid is detected by adding some caustic potash to 10 grms. of butter fat and incinerating in a platinum dish. The ash is acidified with hydrochloric acid, and tested with turmeric paper.

[1] With regard to Gottlieb's method cp. *Zeit. f. Unters. Nahr. u. Gen.* 1905, x. 287; Hesse, *Chem. Zentralblatt*, 1905, i. 124. [2] Cp. Röhrig, *Molkerei Zeit.* 1907, 1303.

Richmond and *Harrison*[1] (using a slight modification of *Thomson's* method) recommend the following process:—About 25 grams of butter are weighed in a stoppered cylinder; enough water is added to make with the water already present 25 c.c., and then 10 to 15 c.c. of chloroform are added. The contents of the cylinder are warmed, mixed, and allowed to separate; an aliquot portion of the aqueous solution is drawn off (each c.c. contains the boric acid in 1 gram of butter), made alkaline, evaporated, ignited, and the ash extracted with hot water. The solution is made neutral to methylorange, boiled to expel carbon dioxide, and titrated with standard alkali after the addition of glycerol. That part of the ash which is insoluble is free from boric acid. For further details and improvements of this process (suggested by *Warren*) the original paper must be consulted.[2]

A more accurate gravimetric method for the determination of boric acid is given by *Partheil* and *Rose*.[3] This method has, moreover, the advantage that the boric acid can be obtained in substance.[4]

Opinions differ as to the harmlessness (or otherwise) of boric preservatives. Although this subject would appear to lie beyond the scope of this work, yet *Wiley's*[5] summary may be reproduced here. "It appears that both boric acid and borax when continuously administered in small doses for a long period, or when given in large quantities for a short period, create disturbance of appetite, digestion, and health." In order to show the extensive use made of boric acid the following notes taken from the Government Laboratory Report[6] may be added: Boron preservatives were found in 53·5 per cent of Canadian butters, 93·8 per cent of French butters, 93·6 per cent of Belgian butters, 83·3 per cent of Australian butters, 84·4 per cent of South American butters, 79·5 per cent of New Zealand butters; the percentages refer to the number of samples taken. Butters from southern countries in particular contained a preservative in excess of the amount recommended as the limit by the "Committee on the Preservatives in Food."

Glucose.—In the United States glucose is used as a preservative for export butter.[7] It is detected by washing the sample repeatedly with hot water and testing the aqueous layer with *Fehling's* solution. The fact should not, however, be overlooked that a *slight* reduction may be caused by milk-sugar or some of the albuminoids.

Salicylic acid is sometimes used to preserve butter.[8] It is detected

[1] *Analyst*, 1902, 179. [2] *Ibid.* 1902, 182.

[3] *Berichte*, 1901, 3611.

[4] For the German official method cp. Fendler, *Chem. Zeit.* 1906, 108; *Zeit. f. Unters. Nahr. u. Genussm.* 1906, xii. 137; *ibid.* 1908, xvi. 209.

[5] *Influence of Food Preservatives and Artificial Colors on Digestion and Health—I. Boric Acid and Borax.* By H. W. Wiley: Washington, U.S. Department of Agriculture, 1904. Cp. a criticism of Wiley's Report by Liebreich (Berlin, 1906, August Hirschwald) and L. Spiegel, *Chem. Zeit.* 1907, 14.

[6] *Journ. Soc. Chem. Ind.* 1907, 1031.

[7] Crampton, *Journ. Amer. Chem. Soc.* 1898, 201; *Analyst*, 1898, 130.

[8] *Journ. Soc. Chem. Ind.* 1887, 670; *Zeit. f. Unters. Nahr. u. Genussm.* 1908, xvi. 209.

by shaking the sample with twice its volume of 20 per cent alcohol and a few drops of dilute ferric chloride. In the presence of salicylic acid the aqueous layer shows a violet tint.[1]

Formalin (formaldehyde) is best detected by *Hehner's* method in the form given to it by *Richmond* and *Boseley*:[2] Add to the aqueous liquor obtained when butter is melted, a drop of milk, and pour the mixture carefully on to the surface of concentrated sulphuric acid contained in a test-tube. In the presence of formalin a blue ring will appear at the zone of contact of the two liquids. A trace of ferric chloride renders the reaction far more distinct. The German official method directs to place 50 grms. of butter in a 250 c.c. flask together with 50 c.c. of water, to warm the mixture on the water-bath, and to distil off 25 c.c. in a current of steam. To 10 c.c. of the distillate 2 drops of an ammoniacal solution of silver nitrate are added, and the mixture allowed to stand in the dark. The presence of formalin is inferred from the reduction of the silver nitrate. (The reaction described above is a general reaction of formaldehyde with proteins.) This method is, however, not free from objection, since butter made from ripened cream may contain volatile silver-reducing substances.[3]

A new preservative, sold commercially, consists of a mixture of glucose and formic acid to which a small quantity of an ester is added, in order to mask the smell. Since at least 0·05 per cent of formic acid is necessary to act as a preservative, its detection is not difficult (*Richmond*[4]).

Benzoic Acid and Benzoates.—These preservatives are now used on the Continent, especially for margarine.[5] From the extensive investigations of *Wiley*[6] the conclusion has been drawn that "in the interest of health benzoic acid and benzoate of soda should be excluded from food products." Since benzoic acid is volatile with aqueous vapours, a slight increase of the Reichert-Meissl value is caused thereby. This may be of special importance in the examination of margarine for the legally permissible limit of added butter. Benzoic acid is detected in the first instance by a somewhat high acid value of the butter fat. It will be best identified by isolating benzoic acid in substance,[7] and by the odour of its ethylester.

Fluorides have recently been used as preservatives, especially for Brittany butter.[8] A "butter preservative" is sold there which contains about 98 per cent of sodium fluoride.

The presence of fluorides is detected by melting about 50 grms.

[1] Cp. also Barthe, *Bull. Soc. Chim.* 1894, 516.

[2] *Analyst*, 1895, 155; 1896, 92, 94, 157.

[3] Cp. Mayrhofer, *Zeit. f. Unter. Nahrgs. u. Genussm.* 1898, xv. 552.

[4] *Analyst*, 1908, 116; cp. *Zeit. f. Unter. Nahrgs. u. Genussm.* 1898, xvi. 226.

[5] Bemelmans, *Zeit. f. Unters. Nahrg. u. Genussm.* 1907, xiii. p. 492; Grimaldi, *Chem. Zeit.* 1908, 794; Lehmann, *ibid.* 1908, 949.

[6] *Influence of Food Preservatives and Artificial Colors on Digestion and Health—IV. Benzoic Acid and Benzoates.* Washington, 1908.

[7] Cp. J. de Brevans, *Journ. Pharm. Chim.* 14 (10), 438; A. E. Leach, *Zeit. Unters. Nahrg. u. Genussm.* 1905, ix. 50; A. Röhrig, *ibid.* 1908; W. v. Genersich, *ibid.* 1908, xvi. 209; Halphen, *Journ. de Pharm et de Chim.* 1908, 201; L. Robin, *Ann. chim. anal.* 1908 (13), 431.

[8] O. and C. W. Hehner, *Analyst*, 1902, 173.

of butter, separating the aqueous layer, rendering it alkaline, and evaporating the latter to dryness. The ignited residue is then treated in a platinum crucible with strong sulphuric acid, the crucible being covered with a wax-coated watch-glass, having a mark scratched in the wax. The crucible is heated on a sand-bath for two hours. In the presence of even one milligram of calcium- or sodium-fluoride the glass will be found distinctly etched.

Since in the presence of a boric preservative boron fluoride is evolved by strong sulphuric acid, the formation of boron fluoride must be prevented by the use of dilute sulphuric acid; as long as the amount of boric acid does not exceed five times the amount of the fluoride present, the etching of the glass can be obtained. It is, however, preferable to remove the boron compounds at first. This is done by separating the aqueous liquor from 50 grms. of butter, adding calcium chloride, and heating to boiling after a small excess of sodium carbonate has been added. The precipitate (consisting of calcium borate, calcium fluoride, calcium carbonate, calcium phosphate, and perhaps traces of sulphate) is filtered off, ignited, and the residue treated with hot dilute acetic acid to remove the carbonate, borate, and phosphate. The residue is then filtered off, ignited, and treated with strong sulphuric acid as described above.

4. **Colouring Matters.**—Butter has no special colour of its own. That made during the time when the cows are on grass is yellow, whereas in winter when the cows are stall-fed the butter is almost white.[1] As the public demands a yellow butter, the product is, as a rule, coloured artificially before being placed on the market. The use of colouring matters, therefore, is not prohibited. (Butter which is naturally yellow is rapidly bleached when exposed to light and air.)

Foreign colouring matters, "butter colouring," are detected by shaking the melted butter with alcohol. In presence of foreign colouring matters the alcoholic layer becomes tinted, whereas natural butter leaves the alcohol colourless.

Moore[2] and *Martin*[3] recommend the use of a mixture of alcohol and carbon bisulphide. According to *Martin*, 5 grms. of butter are shaken with 25 c.c. of a mixture consisting of 15 parts of methyl alcohol, or ordinary alcohol, and 2 parts of carbon bisulphide. Two layers are formed; the lower one consists of the fat dissolved in carbon bisulphide, the upper alcoholic layer contains the colouring matter.

Stebbins,[4] however, has pointed out that the small quantity of fat retained by the alcoholic layer may interfere with the subsequent examination, and that "carotin," the colouring matter from carrot juice, is more easily soluble in carbon bisulphide than in alcohol.

[1] In this connection it may be interesting to note that in some Swiss farms having an abundant growth of *Leontodon* and *Ranunculus*, the cows gave butter of such intense yellow colour that suspicion was aroused; the butter obtained after the second grazing was very much paler. In the United States also intensely yellow butter is met with.

[2] *Analyst*, 11, 163.

[3] *Ibid.* 12, 70.

[4] *Journ. Amer. Chem. Soc.* 1887, 41.

He substitutes, therefore, the following process:—Melt 50 grms. of the sample in a beaker on the water-bath, stir into the melted mass 5 to 10 grms. of finely powdered fuller's earth, agitate thoroughly for two or three minutes, and allow to settle out completely whilst warm. Drain off the bulk of the fat, add 20 c.c. of benzene, stir well, allow to deposit, and decant the solution through a filter. Repeat this process until the fat is completely removed, and wash the precipitate on the filter with benzene. Test the filtrates for carotin. Dry the precipitate on the water-bath, and boil out three times with about 20 c.c. of 94 per cent alcohol. Evaporate the alcoholic extracts in a tared dish, dry at 100° C., and weigh the residue. The residue obtained by either method is then examined by means of special reactions for the colouring matter suspected to be present.

Turmeric (*curcuma*) and **annatto** (notwithstanding the disgusting method by which the latter is prepared) are at present chiefly used in France. A preparation for colouring butter is sold there under the name of "jaune gras" ("fat yellow"), made by digesting annatto with sesamé oil and then adding turmeric.

Turmeric is indicated by the appearance of a brownish-yellow colouration on adding a few drops of ammonia, and of a reddish-brown colouration on subsequently adding hydrochloric acid.

Annatto is identified by a reddish-brown residue, which dissolves in concentrated sulphuric acid with production of a blue colour.

In the presence of *saffron* an orange-coloured precipitate is obtained on dropping lead acetate into the aqueous solution of the residue.

Harmless colouring matters are turmeric, annatto, carotin, marigold extract, and saffron. With regard to the last colouring matter it should, however, be noted that exhausted saffron, coloured yellow with an aniline dye, is frequently sold.

Aniline colours are, as a rule, poisonous, and should not be used for colouring butter.[1] A comprehensive scheme for testing for the various colouring matters has been worked out by *Leeds*.

Leeds[2] dissolves 100 grms. of butter in 300 c.c. of pure petroleum ether, of 0·638 specific gravity, in a separating funnel, draws off the curd and water, and washes several times with water, using about 100 c.c. The solution of butter fat is then kept at 0° C. for about twelve to fifteen hours, so that the bulk of the solid glycerides may crystallise out. The liquid fat is poured off and shaken with 50 c.c. of decinormal alkali, to remove the colouring matters from the ethereal solution. The aqueous layer is drawn off and carefully titrated with hydrochloric acid, until just acid to litmus. The colouring matters, containing a minute quantity of fatty acids, are thus precipitated; the precipitate is transferred to a tared filter, washed with cold water, dried, and weighed.

For the discrimination of the several colouring matters the precipitate is dissolved in alcohol and two or three drops of the

[1] R. W. Cornelison, *Journ. Amer. Chem. Soc.* 1908, 1478. [2] *Analyst*, 1887, 150.

solution tested with an equal quantity of the reagents given in the following table :—

Reactions of Colouring Matters

Colouring Matters.	Concentrated H_2SO_4	Concentrated HNO_3	$H_2SO_4 + HNO_3$	Concentrated HCl.
Annatto	Indigo blue, changing to violet	Blue, becoming colourless on standing	Same	No change, or only slight dirty yellow and brown
Annatto + decolourised butter	Blue, becoming green, and slowly changing to violet	Blue, then green and bleached	Decolourised	No change, or only slight dirty yellow
Turmeric [1]	Pure violet	Violet	Violet	Violet, changing to original colour on evaporation of HCl
Turmeric + decolourised butter	Violet to purple	Violet to reddish violet	Same	Very fine violet
Saffron	Violet to cobalt blue, changing to reddish brown	Light blue, changing to light reddish brown	Same	Yellow, changing to dirty yellow
Saffron + decolourised butter	Dark blue, changing quickly to reddish brown	Blue, through green to brown	Blue, quickly changing to purple	Yellow, becoming dirty yellow
Carrot	Umber brown	Decolourised	Do. with NO_2 fumes and odour of burnt sugar	No change
Carrot + decolourised butter	Reddish brown to purple, similar to turmeric	Yellow, and decolourised	Same	Slightly brown
Marigold	Dark olive green, permanent	Blue, changing instantly to dirty yellow green	Green	Green to yellowish green
Safflower	Light brown	Partially decolourised	Decolourised	No change
Aniline yellow	Yellow	Yellow	Yellow	Yellow
Martius yellow	Pale yellow	Yellow, reddish precipitate. Magenta at margin	Yellow	Yellow, precipitate treated with NH_3 and ignited; deflagrates
Victoria yellow	Partially decolourised	Same	Same	Same, colour returns on neutralising with NH_3

[1] Ammonia gives with turmeric a reddish-brown colour which reverts to the original colour on driving off the ammonia

According to *Leffmann*,[1] methylorange is extensively used in the United States, especially for "oleomargarine." The colouring matter is extracted as described above and tested with dilute acid, when the well-known red tint will appear.

Geisler[2] states that annatto is now largely replaced in the United States by a yellow azo dye, which is used in combination with an orange dye (methylorange?). The dye can be extracted from the fat by agitating with fuller's earth from which the colouring matter in its turn can be extracted by boiling alcohol. The isolated dye dissolves in concentrated sulphuric acid, giving a yellow colouration which changes to red on the addition of water. (Methylorange does not behave in the same manner with fuller's earth.)

In the United States red palm oil also has been used as a colouring matter, the palm oil being incorporated with the help of cotton seed oil. (This colouring matter was chiefly used in the manufacture of "oleomargarine.") As the employment of this colouring matter is now prohibited by law, the methods which had been proposed for its detection need not be discussed here[3] (cp. also Vol. III. Chap. XV.).

Grünhut[4] proposes to detect colouring matters by dyeing wool with the extract. He saponifies the sample in the cold (Vol. I. Chap. II.), evaporates off the petroleum ether and the bulk of the alcohol, dissolves the residue in water and acidulates slightly (so that the fatty acids just commence to separate), renders slightly alkaline with sodium carbonate, and heats to boiling after adding some wool. Dimethylamidoazobenzene cannot be detected by the dyeing test; its presence must be proved spectroscopically, after the colouring matter has been extracted from the soap solution by means of petroleum ether. It should be noted also that annatto dyes wool yellow.

Further notes on colouring matters will be found, Vol. III. Chap. XV., under the heading "Edible Fats."

Butter colours are similarly examined, using, of course, a smaller quantity of the sample. About 5 grms. are dissolved in 20-25 c.c. of petroleum ether, and treated with 10 c.c. of a 4 per cent solution of potash.[5]

In commerce butter is not merely valued by its purity (as ascertained by the tests described in the foregoing lines, and the chemical tests for butter fat to be described below), but its value depends also to a considerable extent on its flavour and taste. A proper valuation

[1] Second annual report of the Dairy and Food Commissioner of Pennsylvania.
[2] *Journ. Amer. Chem. Soc.* 1898, 110.
[3] Crompton and Simonds, *Journ. Amer. Chem. Soc.* 1905, 270.
[4] *Chem. Centr. Blatt.* 1898, ii. 943.
[5] The following formulæ for butter colours have been taken by *Leffmann* from a *Druggist's Circular*:—

Extract of Annatto	10 ounces.	Annatto seed, bruised	10 parts.
Turmeric	5 ,,	Turmeric	3 ,,
Logwood chips	2½ ,,	Ammonium carbonate	1 part.
Cotton seed oil	1 gallon.	Cotton seed oil	75 parts.
		Lard	10 ,,

of butter on the strength of the last two properties hardly belongs to the province of the analytical chemist, as it requires a good deal of practice, which is not based on chemical evidence.

Different countries and even different provinces of one and the same country require differently flavoured butters; and their value is judged regularly in commerce, without having recourse to chemical analysis.

In this connection it may be pointed out that the peculiar aroma of a good butter is due to the action of a bacterium which gives rise to the formation of the flavouring substance during the ripening of the cream. That this is the case is shown by the general experience that the desired butter aroma does not appear in sweet cream butter, such butter having what is termed a "flat" (insipid) taste. A bacterium of this kind was first isolated by *Storch*. *Weigmann* described two forms or races, one of which develops an exquisite flavour and aroma, but yields a butter which does not keep well, whilst the second race develops less aroma but the butter keeps better. The cultivation of cream-ripening bacteria has been considerably advanced in America by *H. W. Conn*.[1] Laboratory experiments having demonstrated that a particular butter bacillus can produce a pleasant flavour, if inoculated into the cream during the process of ripening under such conditions that it can grow rapidly, pure cultures of this bacillus were distributed amongst numerous dairies. By this means the "June flavour," which had hitherto only been met with in butter of certain districts during a short season of the year, can now be produced artificially. This flavour is stated to be retained in the butter even for a longer period than the flavour which is obtained without such aid in ripening. In addition to the fine flavour a somewhat enhanced keeping property is said to be imparted to the butter.

"Fishy" butter obtained (in Norway) from cows fed on fish meal,[2] "sandy" butter (which contains undissolved salt granules), and other kinds of butter having an objectionable flavour will naturally be either rejected or must be sold at low prices. Most of the badly flavoured butters,[3] as also those which are mouldy, spotty,[4] discoloured, etc., are re-worked and sold as renovated butter.

"Renovated" butter or **"process"** butter (French—*Beurre renové*, *Beurre rebroyé*; German—*Aufgefrischte Butter*, *Renovierte Butter*) is manufactured in large quantities in the United States. It is stated that during 1902 the production of "process" butter amounted to 5,879,833 lbs., equal to about half the quantity of margarine

[1] Cp. *Bacteria in Milk and its Products*. London, 1903: Rebman, Limited.

[2] Badly flavoured colonial butter has also been termed "fishy" butter or butter suffering from "fishiness." This is stated to have been caused by the contact of the milk or cream with rusty utensils. Others have ascribed this defect to the action of a micro-organism acting on the proteins in butter. The growth of this organism is said to be prevented by "salting" the butter or by cold storage.

[3] Cp. H. Weigmann, *Landw. Jahrb.* 1908 (37), 261.

[4] The appearance of spots ("marbled butter") seems to be due to the defective removal of butter-milk, or to the fact that the salt has not been evenly distributed in the butter.

("oleomargarine") made in the United States. It is manufactured from unsaleable "rancid" butter, by melting and separating the butter fat from the aqueous solution and the curd. The fat is next blown with air to remove the objectionable flavour, and then quickly cooled in a current of cold water, so as to prevent the separation of the more liquid portion of the butter ("butter oil") from the more solid portion. The butter fat is then churned with fresh milk to which cultures of suitable bacteria have been added. The milk soon becomes sour and coagulates, thus furnishing an artificial curd, containing about the same proportions of nitrogen as does the curd of genuine butter. It is evident that by chemical methods alone "renovated butter" cannot be distinguished from genuine butter, the fat contained in such butter being, of course, genuine butter fat, and the proportions of the constituents being, as a rule, so regulated as to simulate the composition of a normal butter. This is exemplified by the mean of seventy-five analyses of process butters published by *Crampton*[1] :—

	Maximum.	Minimum.	Mean Value.
	Per cent.	Per cent.	Per cent.
Fat . . .	88·88	68·80	82·05
Curd . .	2·65	0·77	1·47
Ash . . .	7·49	0·97	2·85
Water . .	23·17	8·01	14·44

"Process or renovated butter" is defined by the "Act of Congress of 9th May 1902" as butter which has been subjected to any process by which it is melted, clarified, or refined, and made to resemble genuine butter. Process butter containing any substances foreign to butter or more than 16 per cent of water is classed as "adulterated butter."

Hess and *Doolittle*[2] propose to identify renovated butter by the appearance of the curd, as the curd from process butter is milk-casein, whereas the curd from normal butter is the protein of cream. They further state that renovated butter presents under a polarisation microscope a different appearance from genuine butter. In genuine butter the fat is contained in isotropic, or at any rate in such micro-crystalline form that under the polarisation microscope with moderate magnification no polarising crystals, or at any rate only few, are noticed. Renovated butter shows, on the contrary (like margarine), throughout the whole mass a distinct crystalline structure.[3] For the details the reader must be referred to the original paper, and it need only be added that, according to *Hess* and *Doolittle*, "process butter" does not yield a clear layer of fat on melting, even after some prolonged standing, whereas the fat of pure butter becomes clear soon after melting. This may explain the observation

[1] *Journ. Amer. Chem. Soc.* 1903, 358. [2] *Ibid.* 1900, 150.
[3] Cp. Bömer, *Zeit. f. Unters. Nahrs. Genussm.* 1908, xvi. 27.

that renovated butter (like margarine) is characterised by "spurting" when heated in a pan, whereas genuine butter froths quietly.

Renovated butter does not keep as well as genuine butter.

The production of renovated butter must be carried out with scrupulous cleanliness throughout. The renovated butter works which the author saw in the United States were equipped in an entirely unobjectionable manner. It appears that the production of renovated butter is being adopted in Europe, and several patents for "renovating" have been taken out during recent years.[1]

Siberian and Danish butters in particular appear to be used in Germany for the production of renovated butter, as they suffer in transit and the outer portions become rancid.[2] These outer rancid portions are scraped off and sold as inferior butter ("Kratzbutter," "Staff"), or treated for renovated butter.

Renovated butter is now being admixed (fraudulently) in Germany with fresh butter. The detection of an admixture of renovated to fresh butter is a problem which, in the present state of our knowledge, cannot be solved by chemical means.

The presence of curd and water renders butter far more liable to become rancid than is the case with pure butter fat. Hence in some countries, as in South-West Germany, India, Siberia (for export to Turkey), butter is melted until the butter fat has become quite clear, whereupon the latter is separated from the curd and water. The flavour of such butter ("Schmelzbutter") suffers, however, considerably.

If the temperature employed in melting the butter is too low, the separation of the water and casein does not take place completely, and hence the butter is liable to become rancid. On the other hand, if the temperature in melting be too high, the butter fat acquires a tallowy taste.

The literature dealing with the rancidity of butter is a very voluminous one, but unfortunately a number of writers seem to have confounded butter fat with butter. The conditions influencing the liability of butter fat to become rancid have been fully explained in Vol. I. Chap. I. Although the determination of the free fatty acids in butter fat (acid value of the butter fat) is of little use, since acidity is not coterminous with rancidity, it is still the practice of some analysts to determine the amount of free fatty acids in butter fat in order to arrive at a "measure of rancidity." If a measure of the amount of hydrolysis which a butter fat has suffered be desired, the determination of the acetyl value—indicating in this case the amount of mono- and di-glycerides—will afford the required information.

[1] Belgian patent 172,592; English patent 28,374, 1904; French patent 355,362; English patent 7500, 1907; English patent 28,024, 1907; United States patent 881,929 (W. F. Jensen).

[2] Cp. Goock, *Zeit. f. öffentl. Chem.* 1908, 198.

The conditions favouring the rancidity of butter fall outside the scope of this work, and the reader must therefore be referred to the original papers given in the footnote.[1]

On exposure to light, butter not only loses its yellow colour, but also acquires a tallowy ("lardy") smell and taste.

2. Examination of the Butter Fat

For tables of characteristics see pp. 669-671.
For characteristics of the milk fats from other animals than cows see p. 672.

Pure butter fat consists almost exclusively of triglycerides of fatty acids. Besides triglycerides, it contains cholesterol and some natural colouring matters (lactochromes). The total amount of unsaponifiable matter is less than a half per cent (0·35 per cent, *Bömer*; 0·31-0·41 per cent, *Lewkowitsch*; 0·42 per cent, *Klein* and *Kirsten*;[2] 0·215-0·325 per cent, *Siegfeld*). Lecithin has been stated by various observers to occur in butter fat to the extent of 0·017 or even 0·15 to 0·17 per cent (calculated from phosphoric acid). *Wrampelmeyer*[3] stated 0·007 to 0·033 per cent of lecithin. *Jaeckle*, however, showed that butter fat contains no compound of phosphorus.

The following acids have been identified hitherto in butter fat:— acetic,[4] butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, and oleic. *Wachtel*, as also *Bondzyński* and *Rufi*, stated that butter fat contains hydroxylated acids, and on the strength of their results obtained by the application of faulty methods, *Browne*[5] has even calculated the percentage of hydroxylated acids. Experiments made by the author prove, however, that butter fat contains practically no hydroxylated acids, the low acetyl values found being due to the presence of small quantities of mono- and di-glycerides.

The extraordinarily high percentage of glycerides of soluble fatty acids in butter fat is characteristic, and differentiates it from all other fats.[6]

[1] Schmidt, *Zeit. f. Hygiene u. Infectionskrankheiten*, 1898, 163; Hanus, *Zeit. f. Unters. d. Nahrgs. u. Genussm.* 1900, 324; Hanus and Stocky, *ibid.* 606; Lydia Rabinowitsch, *Jahrbuch d. Chemie*, ix. 237; Crampton, *Journ. Amer. Chem. Soc.* 1902, 711; Orla Jensen, *Jahrbuch d. Chemie*, xii. 363; O. Laxa, *Arch. f. Hygiene*, 1902, 119.

[2] *Zeit. f. Unters. Nahrg. u. Genussm.* 1903, 147.

[3] *Landw. Versuchsstat.* 1903, 437.

[4] Cp. E. Wein, *Inaug. Dissertation*, Erlangen, 1876. Wein claims also to have detected the presence of formic acid in fresh butter fat.

[5] *Journ. Amer. Chem. Soc.* 1899, 613.

[6] Buttenberg (*Zeit. f. Unters. Nahrg. u. Genussm.* 1908, 335) describes a peculiar vegetable oil, said to be obtained from a Chinese seed, which has a remarkably high *Reichert-Meissl* value, viz. 34·85. The examination of this oil, which Buttenberg obtained from Holland under the name "Butter Oil" (!), had the following characteristics:—

The quantity of stearic acid obtained by the method described Vol. I. Chap. VIII. is very small. In an analysis carried out in the author's laboratory with a sample of butter fat of the *Reichert-Meissl* value 28·1, the amount of stearic acid found in the insoluble fatty acids was only 0·49 per cent (see Vol. I. Chap. XII.). The presence of less saturated acids than oleic acid in a normal butter has not yet been proved beyond doubt. *Farnsteiner* has shown that in the butter from a cow fed on cotton meal, traces of linolenic acids were ascertainable. *Partheil and Ferié* stated that less saturated acids than oleic occur in butter fat to a somewhat considerable extent; but as the method by which their presence was determined is not free from serious objections (Vol. I. Chap. VIII.), their statement must be accepted with reserve.

According to *Duclaux*,[1] butter fat contains from 2 to 2·26 per cent of caproic, and from 3·38 to 3·65 per cent of butyric acid. From this he (somewhat arbitrarily) assumes the proportion in which butyric acid stands to caproic in butter fat to be 1·645.

On this basis *Violette*[2] calculated severally the proportions of butyric, caproic, solid volatile, and insoluble fatty acids by proceeding in the following manner:—50 grms. of butter fat are saponified and the volatile acids separated, as in *Reichert's* distillation process. The solid volatile acids are separated by filtration, and their quantity determined after drying;[3] the amount of the insoluble fatty acids is arrived at in the same way. The total quantity of the soluble acids is ascertained by titration with decinormal alkali, and calculated to butyric acid. If A represent this quantity, then the quantities of butyric and caproic acids, B and C, can be calculated on the above stated assumption with the help of the following equations:—

$$B = A \times 0{\cdot}68469$$
$$C = A \times 0{\cdot}41565$$
$$\frac{B}{C} \text{ being} = 1{\cdot}645.$$

Saponification value	234·7
Reichert-Meissl value	34·85
Titration number of the insoluble volatile acids	0·55
Iodine value	64·6
Unsaponifiable matter	0·38 per cent.

Melting point of the eighth crop of crystals from unsaponifiable matter, 179·6-180·6° C.
Melting point of the alcohol recovered from the acetate, 163·7-166·2° C.

The "alcohol" melted after recrystallisation from ethyl alcohol at 177·3 to 178·3° C., and showed under the microscope the characteristic crystal form of phytosterol.

The oil did not give the *Halphen* reaction (for cotton seed oil), but gave positive colour reactions for sesamé oil, although only faintly.

These numbers suggested to me the conjecture that this new oil is an artificially prepared mixture of vegetable oils (containing sesamé oil) with butyrin or caproin, designed to serve as a butter adulterant. Buttenberg, however (in a private communication to me), declared that there was no reason to doubt that the new oil was a natural one. The presence of butyrin or caproin can be easily ascertained; the melting point of the "alcohol" and its "acetate" in the unsaponifiable matter appear, however, peculiar.

An oil remarkable for a still higher Reichert-Meissl value—viz. 35·31—is spindle tree oil from the seeds of *Evonymus europæa*, L. Cp. Appendix to Vol. II. and table facing p. 192.

[1] *Compt. rend.* 102, 1022. [2] *Journ. Soc. Chem. Ind.* 1890, 1157.
[3] With regard to errors caused by this procedure cp. Vol. I. Chap. VIII.

Physical and Chemical Characteristics of Butter Fat

Specific Gravity.			Solidifying Point.		Melting Point.[1]		Saponification Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·936-0·940	Hager	19-20	Wimmel	29·5-34·7	Bell	227	Köttstorfer,	26·0-35·1	Hübl
37·8 (100° F.) (water 37·8° = 1)	0·911-0·913	Bell	20-23	Thoerner	29·4-33·3	Cameron		Valenta,	25·7-37·9[4]	Wollny
,,	0·910-0·913	Thorpe			28-33	Thoerner	(221·5-233·4)	Moore,	29·0-43	O. Jensen
40 (water at 15·5 = 1)	0·9041	Allen						Allen, etc.	30·6-50·3	van Rijn
100 (water at 15 = 1)	0·865-0·868	Koenigs					225-230	Thoerner		
100 (water at 15·5 = 1)	0·867-0·870	Allen					221-233	Seyda and Woy[2]		
100 (water at 100 = 1)	0·901-0·904	Wolkenhaar					219·7-232·6	Thorpe[3]		
,,	0·9094-0·9140	Bell					(Cp. p. 713)	K. Fischer		
,,	0·9105-0·9138	Muter								
,,	0·9099-0·9132	Allen								

[1] According to Meyer (*Milch-Zeit.* 1892, 49) the melting point of cow butter is lowered by food consisting of easily digestible carbohydrates, but raised by straw, oil cakes, or sour fodder.

[2] Silesian butters. [3] Calculated by me from the "saponification equivalents" of 357 English butters. [4] 56 samples, mean 33·32.

Physical and Chemical Characteristics of Butter Fat—continued

Reichert Value.		Thermal Test.		Refractive Index.		
		Heat of Bromination.				
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	°C.	Observer.	At °C.		Observer.
14 (12·5-15·2)	Reichert, Moore, Allen, etc.	6·6-7·0 9·5	Hehner and Mitchell Broomwell and J. L. Meyer	25 60	1·4590-1·4620 1·445-1·448	Wollny. Thoerner
Reichert-Meissl Value.				Oleo-refractometer.		
				"Degrees." At 45° C.		Observer.
20·63-33·15	Cp. pp. 686-688.			−29 to −31 −25 to −31		Jean Pearmain
				Butyro-refractometer.		
				At °C.	Scale Divisions.	Observer.
				25	52·5	Skalweit
				25	49·5-54	Wollny
				35	44·8-47	Besana
				40	41-42	Mansfeld
				40	40·5	Beckurts and Seiler
				40	40·5-44	Delaite
				45	37·6-42·5	Thorpe
				45	38·9-45·5	van Rijn

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.[1]	
Per cent.	Observer.	At 37·75° C. (water 15·5° C. = 1).	Observer.	°C.	Observer.	°C.	Observer.
87·5	Hehner	0·9075-0·9085	Leonard	35·8	Hübl	38	Hübl
86·45-89·8	Bell	0·90919-0·91357	Bell	37·5-38	Paris Municipal Laboratory	41-43 and 43-45	Bensemann
				33-35	Thoerner	38-40	Thoerner

Physical and Chemical Characteristics of the Insoluble Fatty Acids—continued

Neutralisation Value.[2]		Iodine Value.		Heat of Bromination.		Refractive Index.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
210-220	Thoerner	28-31	Thoerner	6·2	Hehner and Mitchell	1·437-1·439	Thoerner

[1] Butter from cows fed on cotton seed cakes has a considerably (by 8° to 9° C.) higher melting point (Lupton, *Journ. Amer. Chem. Soc.* 1891, 134).

[2] The neutralisation values of the fatty acids obtained after distilling off the volatile fatty acids by Reichert's process were found 213·3 to 218·9 (Henriques).

Characteristics of the Milk Fats from other Animals

Milk Fat from	Specific Gravity. At 15° C.	Specific Gravity. At 100° C.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable.	Refractive Index.	Unsaponifiable Matter. — Per cent.	Observer
Goat [1]	0·9312	0·8669	24·31	27-38·5	221·6	30·4-34·6	23·1-25·4	86·5-87·3	1·4596	...	Solberg
,,	...	...	31	36·5	...	...	28·6	...	...	...	Pizzi
,,	...	0·8651	...	...	233·9-241·3	21·1-28·7	21·1-24·3	...	...	...	K. Fischer [2]
,,	...	...	...	...	226·1-242·4	25·2-38·9	17·2-29·1	87·8	...	...	Sprinkmeyer and Fürstenberg [3]
,,	...	0·8637	...	...	235-245	24·7-33	20·6-26·5	...	...	...	Paraschtschuk [1]
Sheep	...	...	...	29-30	...	...	32·9	...	...	...	Pizzi
,,	...	...	...	...	235·1-237·1	30·2-32·7	28·8-32·3	...	...	...	Don [4]
Mare	...	...	...	...	...	...	11·2	...	...	...	Pizzi
Ass [5]	...	...	...	...	...	...	13·1	...	...	...	,,
Buffalo	...	...	29	38	...	...	26·2	...	...	...	,,
,, (Bulgarian)	...	0·8692	...	...	229·0	36·75	34·2	88·19	...	...	Petkow [6]
Reindeer	0·9428	0·8640	34-39	37-42	219·2	25·1	31·4	86·89	1·4647	...	Solberg
Gamoose (Buffalo)	...	...	...	...	220·4-231·7	32-35	34·7-35	86·9-87·5	...	...	H. D. Richmond
									Oleo-refractometer. "Degrees."		
Camel	...	...	...	38 [7]	208	55·1	...	...	−20	...	Vamvakas [7]
Woman	...	0·870	...	...	218·4	43·4	15·8 [8]	89·2	...	4·68 [9]	Sauvaitre [10]

[1] *Milchw. Centralblatt.* 1907, 507.

[2] *Zeit. f. Unters. Nahrg. u. Genussm.* 1908, xv. 12. Butyro-refractometer, 36·5-41·0 "degrees" at 40° C. Titration number of insoluble volatile acids, 6·85-9·80. Mean molec. weight of the non-volatile acids, 253·6-269·3. Butyro-refractometer of these acids, 28-33·1 "degrees" at 40° C.

[3] *Zeit. f. Unters. Nahrg. u. Genussm.* 1907, xiv. 390; 1908, xv. 413. Butyro-refractometer at 40° C., 40·4-43·8 "degrees." Titration number of insoluble volatile acids (see p. 694), 3·15-8·00. Mean molec. weight of non-volatile fatty acids, 244·5-266·5. Butyro-refractometer of these non-volatile acids, 29·2-33 "degrees" at 40° C. Cp. also Dons, *Zeit. f. Unters. Nahrg. u. Genussm.* 1908, xv. 73.

[4] *Zeit. f. Unters. Nahrg. u. Genussm.* 1908, xv. 73. Titration number of insoluble volatile acids (see p. 694), 5·2-6·6. Butyro-refractometer at 40° C., 38·2-38·9 "degrees."

[5] The proportion of fat in the milk varies, according to Wagner, from 8·1 to 0·1 per cent, and even less (*Zeit. f. Unters. Nahrg. u. Genussm.* 1906, xii. 659; 1908, xvi. 175).

[6] *Zeit. f. Unters. Nahrungs- u. Genussm.* 1901, 826.

[7] *Chem. Centr.* 1905, ii. 1130; *Analyst*, 1905, 370.

[8] Total volatile acids, 4·41 per cent. Ratio of butyric acid to caproic acid, 2·4 : 1.

[9] A normal cow butter gave to Sauvaitre 1·58 per cent of unsaponifiable matter.

[10] *Annal. Chim. analyt.* 1902, 143. Cp. also A. Jolles, *Chem. Zeit.* 1903, 505.

In the following table *Violette's* results are reproduced :—

Fatty Acids.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyric acid . .	6·07	5·33	5·50	5·05	4·62	4·80	4·76	4·37
Caproic acid . .	3·66	3·23	3·34	3·06	2·80	2·92	2·89	2·65
Solidvolatile acids	2·85	3·00	2·80	3·00	2·90	2·40	3·00	2·95
Non-volatile acids .	82·28	82·63	82·87	83·20	84·32	84·31	83·83	84·62
Total . .	94·76	94·19	94·41	94·31	94·64	94·43	94·48	94·59

By ascertaining finally the mean molecular weights of the solid volatile and of the non-volatile acids, *Violette* obtained all the data necessary for calculating the composition of the butter fats. This is given in the following table :—

Glycerides.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyrin . . .	6·94	6·09	6·28	5·76	5·28	5·49	5·45	5·00
Caproin . . .	4·06	3·58	3·70	3·39	3·09	3·23	3·10	2·94
Glycerides of solid volatile acids . . .	3·06	3·22	2·96	3·16	3·06	2·53	3·16	3·15
Glycerides of non-volatile acids . . .	85·98	86·62	86·60	86·93	88·10	88·10	87·60	88·42
Difference . . .	0·04	0·49	0·46	0·76	0·47	0·65	0·69	0·49
	100	100	100	100	100	100	100	100

Subjoined is a table showing the composition of butter fat, calculated by the author from the data given by the observers named :—

Glycerides.	J. Bell.	W. Blyth.	Spallanzani.[1]
	Per cent.	Per cent.	Per cent.
Butyrin . . .	7·012	7·7	5·080
Caproin . . .	2·280	0·1	1·020
Caprylin and caprin .			0·307
Olein	37·730	42·2	93·593
Palmitin, stearin, etc. .	52·978	50·0	
	100	100	100

How the theoretical composition of a butter fat may be calculated from the numbers obtained on examining it by the quantitative

[1] *Le Staz. Sperim. Ita.* 23, 417 (1890).

tests, has been shown above (Vol. I. Chap. XI.). In the example given there the volatile fatty acids were found by difference; the volatile acids may be further resolved into soluble volatile and insoluble volatile acids (*Violette's* solid volatile acids; cp. *Müntz and Coudon's* as also *Polenske's* methods, p. 700). The calculated mean molecular weight of the mixed volatile acids was 114. In the example, given Chap. XII., stearic acid was determined direct; the sum of all other saturated fatty acids was obtained by difference.[1]

Müntz and Coudon[2] gave as the total amount of *soluble volatile acids*, expressed as butyric acid, the following percentages:—

Rich butter	6·50 per cent.
Medium butter . . .	5·50 ,,
Poor butter	5·25 ,,
Very poor butter . . .	5·00 ,,
Exceptionally poor butter . .	4·90 ,,

It should be noted that the quality of the butter is judged here by the percentage of soluble volatile acids; this factor would not be recognised in commerce as the guiding principle, since the flavour and taste of a butter, and hence its commercial value, do not depend exclusively on the larger or smaller amount of soluble volatile acids, which only chemical analysis reveals. The amount of *insoluble volatile acids*, also expressed in terms of butyric acid, was found by *Müntz and Coudon* in two butters to lie between 1·74 per cent and 1·96 per cent.

Müntz and Coudon give for the relation (see p. 699)—

$\frac{\text{Insoluble volatile acids}}{\text{Soluble volatile acids}} \times 100$, the mean number 12·04, the minimum being 9·1 and the maximum 15·6 (cp. also below, p. 698).

From the foregoing numbers it will be gathered that butter fat is distinguished from all other fats by its high proportion of butyric acid.

The mean molecular weights of the soluble volatile acids of butter fats, having the *Reichert-Meissl* values 26·3 to 27·5, were stated by *Juckenack and Pasternack*[3] to be 95·1 to 98·3. *W. Arnold*[4] gives 98 as an average; *Siegfeld* 98·4 to 103. These figures refer to the volatile acids as obtained in the 110 c.c. distillate from 5 grams of butter fat in the *Reichert-Meissl* (*Reichert-Wollny*) test. The number 98 proves clearly that, besides butyric acid, some higher volatile acid or acids are dissolved in the aqueous solution of the volatile acids.

The mean molecular weight of the *insoluble volatile acids* has been given by *Siegfeld* as lying between 177 and 207; but, as he himself points out, the method by which these mean molecular weights have been determined is so inaccurate that no reliance can be placed on those figures.

[1] Cp. also Fleischmann and Warmbold, *Zeit. f. Biologie*, 4 (1907), 375. Siegfeld, *Milchw. Zentralbl.* 1907, 288; *Chem. Zeit.* 1908, 505.

[2] *Annales de l'Institut National Agronomique*, Paris, 1904.

[3] *Zeit. f. Unters. Nahr. Genussm.* 1904, 1204. [4] *Ibid.* 1905, 841.

The mean molecular weights of the *insoluble acids* fluctuate between 258 and 266, the lowest number being, of course, due to a fat having the highest *Reichert* value and the highest being due to a fat having the lowest *Reichert* value. It may, however, be pointed out already here that the conclusions which various observers have attempted to draw from the mean molecular weight of the insoluble fatty acids as to the composition of the (nearly) 94 per cent of insoluble fatty acids are hardly valid. For any number of mixtures of fatty acids from lauric upwards to arachidic can be present in butter fat, all having mean molecular weights from 258 to 262.[1] An investigation which the author has undertaken shows that some butters are richer in arachidic acid than others, which, on the other hand, seem to contain larger amounts of myristic acid. It is to be hoped that a closer study of the insoluble acids will lead to a more intimate knowledge of the composition of butter fat, and will incidentally furnish analytical means to reveal adulterations of butter, which hitherto escape detection. For most of the usual methods in vogue deal with the volatile acids only, without taking any detailed notice of the composition of the insoluble acids. The lithium-salt method of *Partheil* and *Ferié*, which was stated to be capable of resolving the insoluble fatty acids into their several components, viz. lauric, myristic, palmitic, and stearic acids, has been shown to be unreliable (Vol. I. Chap. VIII.). Hence the detailed analysis of a butter by those chemists given in the third English edition of this work is not reproduced here.

On treating butter fat with 95 per cent alcohol in the same manner as described under "Lard" (p. 572) glycerides richer in olein pass into the alcoholic solution. The characteristics (1) of the original fat, (2) of the alcohol-soluble portion, (3) of the alcohol-insoluble portion are collated in the following table (*Arnold*[2]):—

	Butyro-refractometer at 40° C. "Degrees."	Saponification Value.	Reichert-Meissl Value.	Mean Molecular Weight of the Soluble Volatile Acids.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids (Polenske's Method).	Iodine Value.	Non-volatile Fatty Acids.			Yield of Alcohol-soluble Portion (from 150 grms. of fat).
							Butyro-refractometer at 40° C. "Degrees."	Neutralisation Value.	Iodine Value.	
										Grms.
1. Original fat	43·7	223·5	25·0	101·4	2·1	42·6	32·4	214·5	45·7	...
2. Alcohol-soluble fat .	40·1	229·9	36·1	100·1	2·70	45·0	34·0	124·0	50·2	36·09
3. Alcohol-insoluble fat	44·3	220·1	21·2	103·1	1·75	41·2	32·0	214·0	43·0	...

It appears very likely that at least some of the triglycerides in butter fat are "mixed" glycerides. The opinion that mixed glycer-

[1] Vol. I. Chap. VIII.

[2] *Zeit. f. Unters. Nahr. Genussm.* 1907, 194; cp. *ibid.* 1908, xvi. 666.

ides occur in butter fat was first pronounced (before oleo-distearin was isolated) by *J. Bell*,[1] on the strength of experiments made by *G. Lewin* in the Government Laboratory. *Bell* stated that a mixed glyceride of the following composition occurs in butter fat :—

$$C_3H_5\begin{cases}O\,.\,C_4H_7O\\O\,.\,C_{16}H_{31}O\\O\,.\,C_{18}H_{33}O.\end{cases}$$

The following facts support this opinion :—If ordinary animal fat is melted and mixed with—say 10 per cent of—butyrin, the latter may be entirely removed by digestion with alcohol, the animal fat being recovered practically in its original condition. If, however, butter fat is treated with hot alcohol, from 2 to 3 per cent only of its weight passes into the alcohol. The fat thus dissolved does not consist of butyrin or caproin, but of a fat which is liquid at 15·5° C., and yields, on saponification, from 13 to 14 per cent of soluble fatty acids, and from 79 to 80 per cent of insoluble fatty acids. The latter have a higher melting point than the mixed insoluble acids obtained from the original butter fat; this tends to disprove the opinion that the low melting point of the extracted fat might be due to an increased proportion of oleic acid in the molecule. These results agree closely with a compound of the above given formula, which *Bell* named oleo-palmito-butyrate of glycerol.

A. W. Blyth and Robertson[2] stated that they isolated from butter fat a crystalline glyceride, to which they ascribe the formula

$$C_3H_5\begin{cases}O\,.\,C_4H_7O\\O\,.\,C_{16}H_{31}O\\O\,.\,C_{18}H_{35}O\,;\end{cases}$$

but no great weight should be attached to this preliminary communication, which has not been followed up by detailed researches.

Further experiments are required to resolve the apparently very complex mixture of glycerides in butter fat into its component parts. In the present state of our knowledge the method of fractional crystallisation from solvents (cp. Vol. I. Chap. XII.) offers the best hope of success.

In order to prepare butter fat for the subsequent examinations, the sample of butter is melted in a porcelain dish at a temperature of about 50° C., until the upper layer has become perfectly clear. The supernatant fat is then decanted through a filter in the water oven.

It has been pointed out already that the adulteration of butter is at present practically confined to the admixture of foreign fats with butter fat, since added substances of a non-fatty nature are easily detected.

In view of the fact that so many new methods for testing butter fat are being recommended, it should be emphasised that many

[1] *The Chemistry of Foods*, ii. 44. [2] *Proceed. Chem. Soc.* 1889, 5.

chemists who publish new methods seem to overlook entirely the fact that there is not the slightest difficulty in distinguishing pure butter from margarine, or indeed from any other fat.[1]

Before the methods of fat analysis had reached the present state of completeness, margarine was very frequently sold—and is being sold to-day—fraudulently as butter.

At present butter adulteration is practised on a most extensive scale by the admixture, in comparatively small proportions to the total fat, of foreign vegetable and animal fats, such as lard (goose fat), cotton seed stearine, cocoa nut oil, palm nut oil, and chiefly margarine ("oleomargarine"). The last-named fatty compound will be considered more fully under the heading of "Butter Substitutes" in Chapter XV.

Recently there has been sold for the purposes of butter adulteration, especially in Germany, a mixed fat consisting of butter fat, oleomargarine, cocoa nut oil, and cotton seed oil. As large a quantity as 30 per cent of this mixture can be added to certain butters without being detected by the so-called "rapid methods" (refractive index, *Reichert-Meissl* value, insoluble volatile acid number, saponification value, iodine value, etc.). Since, however, the detection of vegetable oils, even down to 5 per cent or 3 per cent, has become comparatively easy (see below), the adulterators have substituted for the above-mentioned mixture oleomargarine or lard, or mixtures of both, churned up with water, without addition of a colouring matter—in short, a margarine consisting of animal fats only.

I append a few analyses of such butter adulterants :—

	I.	II.	III.
Reichert-Meissl value	6·79	0·3	0·2
Titration number of insoluble volatile acids	10·53	...	...
Butyro-refractometer at 45°C. "Degrees"	42·17	...	46·1
Iodine value	23·49	...	...
Saponification value	...	197·3	197·0

Butter adulteration is practised on such extensive lines that legislation [2] has stepped in to protect the genuine article. In this country no butter-substitute, however small the proportion of foreign fat, may be sold without a distinct declaration as to its true nature.

The French "Margarine Law" of the 17th April 1897 prohibits the sale, etc., under the name of "butter" of any substances not made exclusively from milk or cream. The regulations under the Act of 1897 have been amended by the "Adulteration Law" of the 1st August 1905, which imposes severe penalties for (amongst other frauds) attempting to falsify the analytical procedures.

[1] Cp., however, footnote, p. 667.

[2] A. Lavalle, *Die Margarine Gesetzgebung*, Bremen, 1896.—*Report of the Departmental Committee on Butter*, London 1904.

The latest "Margarine Law" in Germany, 1897, as also in Austria, 1901, enacts that a manufacturer of margarine is bound to admix with the oils and fats employed 10 per cent of sesamé oil, for the sake of "ear-marking" such butter, as the recognition of sesamé oil is easy by means of the *Baudouin* test. This Act has, however, not been able to prevent the continuation of adulteration, since the importation of foreign made margarine, in the preparation of which no sesamé oil has been used, cannot be prevented.

The Belgian law demands the addition of 5 per cent of sesamé oil and 0·2 per cent of dry potato starch (reckoned on the fatty matter in the margarine). It also forbids the sale of "abnormal" butter.[1] The definition of the latter has been made still more strict in the Belgian "Margarine Law" of 1903, amended the 21st November 1904.

The new law defines a butter as abnormal in composition if its *Reichert-Meissl* value falls below 28, and if, in addition, it has one of the following characteristics: Butyro-refractometer, at 40° C., above 44 scale divisions ("degrees"); a critical temperature of dissolution (in alcohol of 91·1°, *Gay Lussac*), above 57° C.; specific gravity at 100° C., below 0·865 (it should be noted here that, curiously enough, the law omits to state to what temperature of *water* the specific gravity refers; undoubtedly the specific gravity of water refers to 15° C.); the percentage of "insoluble and solid fatty acids" above 88·5 per cent (by *Hehner's* method[2]); a saponification value below 222.

According to the latest "Adulteration Laws" of the United States butter must contain 82·5 per cent of butter fat and a small proportion of other milk constituents, and may be made with or without common salt, and with or without colouring matter. According to the Act of 9th May 1902 adulterated butter is defined as "a grade of butter produced by mixing, re-working, re-churning, in milk or cream, refining, or in any way producing a uniform, purified, or improved product from different lots or parcels of melted or unmelted butter or butter fat, in which any acid, alkali, chemical, or any substance whatever is introduced or used for the purpose or with the effect of deodorising or removing therefrom rancidity or any butter or butter fat with which there is mixed any substance foreign to butter, with intent or effect of cheapening in cost the product of any butter in the manufacture or manipulation of which any process or material is used with intent or effect of causing the absorption of abnormal quantities of water, milk, or cream."

An Act of Congress of the 1st July 1902 gives as one of the chemical standards for butter fat a *Reichert-Meissl* number not less than

[1] The law defined as "abnormal" a butter, the fat of which showed at least two of the following characteristics:—Scale divisions in the butyro-refractometer (at 40°) higher than 41 "degrees"; critical temperature of dissolution with alcohol of 99·1 per cent, a number exceeding 59° C.; specific gravity at 100° C., below 0·864; Reichert-Meissl value, below 25; percentage of insoluble fatty acids, above 89·5; and saponification value, below 221.

[2] This includes, of course, the unsaponifiable matter.

24, and a specific gravity of not less than 0·905 at 40° C. (water at 40° C. = 1). It should, however, be mentioned here that there are separate Food Laws in the various States of North America which are not in conformity with this Act of Congress.

The Netherlands "Margarine Act" of 1900 defines butter as an article of no fat constituents other than those derived from milk. As this law has not been able to prevent adulteration, a number of farmers and dairy owners have privately combined to guarantee their butter as pure, and placed themselves under the supervision of "Control Stations." The Netherlands Government granted an official mark of guarantee in 1904 to seven Control Stations. Such butter is sold under the name "Dutch Control Butter." An Act, dated 17th June 1905, authorises the use of an official control mark which is issued by the Department of Agriculture.

The Danish "Margarine Law" of 22nd March 1897 punishes adulteration of butter by imprisonment.[1] The supervision in Denmark has been so efficient that no adulterated butter has been exported from that country during recent years. Considerable quantities of butter from Sweden, Norway, and Finland having been shipped to Denmark and sold as Danish butter, an Act of the 26th March 1906 deals with the marking of imported butter, and the adoption of the official mark for butter manufactured in Denmark from pasteurised cream. The importation and sale, etc., of foreign butter bearing any mark which might be mistaken for the official one has been prohibited.

The Swedish "Margarine Law," 1905, prescribes the addition of 10 per cent of sesamé oil to margarine fats. It enacts that persons who produce butter are not allowed to manufacture margarine on the same premises.

The Norwegian "Margarine Law" of 1902 enforces the control of butter manufacture by police and Government dairy inspectors, who have access to every creamery, dairy, or factory, and have the right to take samples for examination. Similarly, the imports and exports of butter are controlled by the Customs.

The Italian "Margarine Law" of 1894 defines butter as genuine (unless there are indications to the contrary) when its *Reichert-Wollny* number is not below 26 : if the number be 20, the butter is considered as adulterated ; and when it lies between 20 and 25, as suspicious. Furthermore, butter is considered as adulterated when it indicates in the butyro-refractometer at 35° C. more than 48 scale divisions ("degrees"), or when its specific gravity is below 0·865 at 100° (water at 15° = 1).

The difficulties that were encountered formerly in the detection of foreign fats in butter have been removed to a considerable extent by the modern methods of fat analysis. But the adulterator has kept pace with the progress of fat analysis, and has succeeded, with very great ingenuity, in preparing mixtures that can only be detected by a com-

[1] More rigorous still is the punishment for adulterating butter in Russia.

bination of several methods. Hence, judiciously prepared mixtures of margarine and cocoa nut oil which formerly could not be recognised by the saponification value and the percentage of insoluble fatty acids alone, are no longer admixed in considerable quantities with butter, since the application of the *Reichert-Meissl* (*Reichert-Wollny*) method immediately discloses the fraud. Yet such mixtures are still being used extensively in small quantities, as even the *Reichert-Meissl* test breaks down when only 10 per cent of margarine are admixed with butter. As the *Reichert* value is a measure of the amount of volatile fatty acids, the author in the first edition of this work expressed the fear that the artificial butter industry might succeed in providing means to prepare butter-substitutes having a correct *Reichert* value. This fear has been realised, for butyric acid, tributyrin, and also amyl acetate are being sold (in 40 per cent alcoholic solution) for that purpose, and even patents have been taken out[1] for the addition of volatile fatty acids to butter fat as also to margarine.[2] Such margarine will most likely find its way into butter, as its chemical characteristics only too plainly suggest fraudulent application, for the volatile acids may not only be used to improve the taste of the fatty material, as the patentees claim, but also to mislead the analytical chemist (cp. "Margarine," Chap. XV.).

Not only does the adulterator keep pace with the progress of chemical analysis, but he even adapts himself with great ingenuity to the methods to which the analysts in the different countries resort, and in particular makes excellent use of the limitations which analysts impose upon themselves (or have imposed on them by their authorities on account of the costs of an analysis) by employing "rapid" methods.[3] To give an example, the application of the refractometric method has been of very great value in the rapid analysis of butter fats, especially for purposes of market control (see below). The adulterator has, however, been able to adapt himself also to this test, as he will always adapt himself to the analyst he has to meet. Moreover, the difficulties of the analytical chemist have been enhanced lately by the employment of cocoa nut oil in the adulteration of butter. Unfortunately, the practices of the adulterator are assisted to a very considerable extent by the natural vagaries in the composition of butter fat, since its chemical composition depends to a great extent on the breed (race) of the cow, the mean temperature of the country where the butter is produced, the stabling, *i.e.* the climatic influence to which the cows are exposed; further, on the nature and quantity of the food supplied, the period of lactation, and the idiosyncrasy of the individual cow. Notwithstanding the enormous amount of investigations that have been carried out in different countries, we are still unable to define the variations within which genuine butter fat may fluctuate. Some investigators followed the changes in the composition of butter fat obtained from a considerable number of cows, so as to eliminate the

[1] English patent 22,458, 1900; German patent 121,657.
[2] English patent 15,649, 1900. [3] Cp. *Jahrb. der Chemie*, xvi. 404.

influence of one individual cow, whereas others (*Klein* and *Kirsten*) are of the opinion that only two factors, namely, food and progress of lactation, are of importance, the other factors exercising a minor influence only, so that the examination of butter fats obtained from a limited number of animals may be considered sufficient. This, however, cannot be admitted as correct, as the influence of stabling on the nature of butter has been shown to be so pronounced that during two different seasons of the year butter fats of very different composition are obtained from one and the same herd of animals.

Owing to these variations in the composition of butter fat, it is at present not possible, by merely carrying out the usual rapid tests, to detect in every given case an admixture of 10 or even 20 per cent (when the original butter had a very high *Reichert* value) of foreign fats. The butter adulterator keeps therefore within the limits of such chemical tests as are from time to time agreed upon by analytical chemists, and hence prepares on a large scale adulterated butters which just keep near the lowest limits, so that the analyst is very frequently placed in the position of having to give a butter the "benefit of the doubt," although he may feel convinced that adulteration has taken place. In this work we are not concerned with the limitations to which the public analysts are subjected, and it will be urged that the examination of butter fat must extend beyond the "quantitative reactions." In case vegetable oils or fats have been admixed with butter in a direct manner, or, in an indirect manner through added margarine, in the manufacture of which vegetable fats have been used, the phytosteryl acetate test will give an unmistakable answer. If, however, animal oils or fats are used as adulterants the uncertainty mentioned above still remains. In order to pronounce on the genuineness of a sample of butter it is, therefore, not only necessary to combine several methods of examination, but also, if need be, to examine the volatile acids, as also the insoluble acids separately.

The methods applicable to the detection of adulteration will be enumerated in the order of their usefulness, and the influence which the different natural factors pointed out above have on the composition of the butter fat will be discussed under each heading.

The literature bearing on the examination of butter is an extraordinarily voluminous one, and still grows. The list of methods detailed below cannot, therefore, lay claim to completeness, although no important and really valuable method will be found missing. A large number of insignificant modifications of known methods and a host of valueless proposals have been deliberately omitted.

For further information reference must be made to special works on butter.[1]

[1] Sell, *Arbeiten aus dem Kaiserl. Reichsgesundheitsamt*, 1886 ; Duclaux, *Le Lait : Étude chimique et microbiologique*, Paris, 1904 ; Girard and Brevans, *La Margarine*, Paris, 1888 ; Besana, *Sui Metodi a distinguere il burro artificiale dal burro naturale*, Lodi, 1888 ; Zune, *Traité général d'analyse des beurres*, 2 vols., Paris et Bruxelles, 1892 ; *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, London, 1904.

Refractometric Examination

The first test that is usually applied in "rapid" analysis is the determination of the refractive index of the butter fat by means of the butyro-refractometer or the oleo-refractometer. The butyro-refractometer will be found more convenient. Thus one is enabled to decide by a glance through the instrument whether a butter is grossly adulterated or whether it need only be regarded with suspicion. Owing to the rapidity with which the observation can be carried out, its importance has been sometimes overestimated, and it should therefore be distinctly remembered that the refractometric examination can only be used as a *sorting* test, and that its indications must be supported by further tests.

The refractive indices of pure butter fats have been given in the table, p. 670. An agreement as to which temperature should be adopted as the standard for the refractometric observations has not yet been arrived at. Some observers choose 25° C., others take 40° C. The latter seems to be the most suitable standard temperature. Others again have adopted 45° C., the temperature employed by *Jean* in the observations with the oleo-refractometer.

All samples which give values lying outside the limits stated in the table must be looked upon as suspicious, or at least as "abnormal," and further examination is required to establish whether a sample is pure or not.

In calculating the position of the critical line found in the butyro-refractometer at 25° C. for another temperature, a correction of 0·55 scale divisions should be made for each degree C.

The following table, compiled on this basis, gives the practical limits for pure butter fats at the corresponding temperatures :—

Temperature. C.	Scale Division.
25	52·5
26	51·9
27	51·4
28	50·8
29	50·3
30	49·8
31	49·2
32	48·6
33	48·1
34	47·5
35	47·0
36	46·4
37	45·9
38	45·3
39	44·8
40	44·2
41	43·7
42	43·1
43	42·6
44	42·0
45	41·5

Delaite,[1] however, has shown that numbers calculated from observations made at an arbitrary temperature are not identical with those observed directly. It is therefore necessary to make the observations at the desired temperature.

If a sample furnishes numbers lying within the values given in the table, p. 670, the conclusion must not yet be drawn that the sample is genuine; for mixtures of margarine and cocoa nut oil can easily be prepared showing the refractive index of a normal butter fat. It is evident that any quantity of such mixture may be added to butter with impunity, in case the refractometric observations alone are held to give a decisive answer.

The assumption of earlier observers, and unfortunately still held by some analysts, that the refraction of butter fat stands in a direct relation to the *Reichert* value—in other words, to the proportion of glycerides of volatile fatty acids (or, to be more correct, to mixed glycerides containing lower fatty acids)—has not been borne out by recent evidence (cp., *e.g.*, table, p. 717). It is quite true that (as in the last stages of the period of lactation [*Farnsteiner* and *Karsch*;[2] *Masson*[3]], or in consequence of climatic conditions [*Holm*, *Kvarup*, and *Petersen*[4]]) the refraction increases with the decrease of volatile acids, but the refraction increases in a much greater ratio with the increase of unsaturated fatty acids; in other words, the higher the iodine value the higher will be the refraction. This becomes evident on examining the numbers which I append in the following table, bearing in mind that butter fats yielding the same amounts of volatile acids may vary in their contents of oleic acid from 10 to 15 per cent:—

Refractive Indices of Fatty Acids and their Glycerides

Acid.	n_D at °C.	Refractive Index.	Glycerides.
Butyric . . .	20	1·39906	1·43587
Caproic . . .	20	1·41635	1·44265
Caprylic . . .	20	1·42825	1·44817
Capric . . .	40	1·42855	1·44461
Lauric . . .	60	1·42665	1·44039
Myristic . . .	60	1·43075	1·44285
Palmitic . . .	80	1·42693	1·43807
Stearic . . .	80	1·43003	1·43987
Oleic	20	1·4620	
	40	1·4546	
	60	1·4471	

It will be gathered that the small "influence" on the refractive index caused by a somewhat higher proportion of volatile fatty acids is obliterated by the greater influence of the unsaturated fatty acids.[5]

[1] *Bullet. de l'Assoc. Belge de Chimistes*, 1894 (5), 145; *Analyst*, 1895, 95.
[2] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1898, 16.
Journ. Soc. Chem. Ind. 1898, 861. [4] *Biederm. Centralblatt*, 1901, 48.
[5] Cp. also Partheil and v. Velsen, *Arch. d. Pharm.* 1900, 261.

This is especially shown to be the case by butter fats obtained from cows fed on linseed cake (perhaps also cotton seed meal). Minute quantities of linseed oil pass into the milk, and consequently into the butter, as is proved by the occurrence of linolenic acid in such abnormal butter fats. Therefore, as *Lobry de Bruyn* has shown first, Dutch butters are frequently met with giving deviations of − 25 to − 30, and even − 21 to − 26, in the oleo-refractometer, although they contained the normal amount of volatile fatty acids and had the proper flavour of good butter.

On the other hand, refractometer figures lying outside the numbers given in the tables do not unmistakably point to adulteration, but they certainly point to an "abnormal" butter. In these cases—as exemplified by "abnormal" Dutch butters[1]—further investigation must show whether the sample under examination is an adulterated butter or not.

Observations on the refraction of butter fats obtained from cows in different districts of the United Kingdom, as also from cows set apart for the purposes of an exhaustive inquiry, so that all the influences affecting the chemical composition of butter fat might be traced, were made by the Government Laboratory.[2] The observed fluctuations in the form of average values[3] are set out in the table, p. 717; but it should be repeated that an overestimation must be carefully guarded against.[4] In order to study the subject in detail the reader must consult the "Bluebook."[3]

The conclusion must be accepted that the indications of the refractometer must be supported by other methods; in the first instance, by the determination of the *Reichert-Meissl* value. Indeed, determination of the refractive index has become now of secondary importance, for reasons stated already (and to be repeated below). But it has been placed first, as the examination by this method requires less than a minute, and has, therefore, come into far greater vogue with analysts than it deserves.

The Reichert-Meissl (Reichert-Wollny) Value

The most valuable index in the chemical examination of butter fat is furnished by the determination of the *Reichert-Meissl* or *Reichert-Wollny* value.

This value is of paramount importance, for the reason that it is not possible to prepare a mixture of any fats likely to be used as butter adulterants without adding very considerable quantities of butter fat,[5] so that the mixture may have a *Reichert-Meissl* value approaching that of normal butter fat, whereas all other "values" can be adjusted by a mixture of fats other than butter fat.

[1] Cp. Lam. *Chem. Ztg.* 1900, 394. [2] Thorpe, *Journ. Chem. Soc.* 1904, 248.

[3] *Report of the Departmental Committee on Butter*, London, 1904.

[4] Therefore the two tables given pp. 844, 845 of the third edition of this work have not been reproduced here.

[5] Cp. footnote, p. 667.

Thus it is easy to prepare mixtures of cocoa nut oil and beef fat (or oleomargarine) having the same refractive index, the same amount of water-insoluble fatty acids, the same saponification value, the same specific gravity, and the same iodine value as a normal butter fat, so that if any one of the criteria mentioned were applied solely, to the exclusion of the others, it would be impossible to differentiate butter fat from a mixture of the two fats named, and consequently it would be possible to add any quantity of this mixture to genuine butter fat without the adulteration being detected. It is therefore preferable to commence the examination of a butter fat with the determination of the *Reichert-Meissl* value.

The *modus operandi* has been fully described in Vol. I. Chap. VI. I omit a very large number of "new processes" which have been proposed from time to time, most of these processes being nothing but modifications and combinations of well-known methods. As an example of a superfluous method, I may mention *Kreis's* modification of *Reichert's* process, since it met with some attention. *Kreis*[1] employs for the hydrolysis of 5 grms. of butter fat 10 c.c. of concentrated sulphuric acid. The experience of several chemists, including the author, has proved that invariably sulphurous acid is liberated, which, of course, must vitiate the results unless the sulphurous acid is removed or otherwise rendered innocuous. The ingenuity of several analysts has been exercised to eliminate the error due to the presence of sulphurous acid; others again have tried to exactly define the strength of the sulphuric acid required so as to avoid formation of sulphurous acid.

In order to prevent the possibility of the formation of ethylic esters in the saponification process, *Leffmann* and *Beam* proposed to saponify by means of caustic soda and glycerin. (It has been shown (Vol. I. Chap. II.) that, provided a sufficient amount of alkali be used, no ethylic esters remain unhydrolysed.) This process has been adopted by several laboratories affiliated to dairies and by the German Imperial "Gesundheitsamt," especially for *Polenske's* method of determining the insoluble volatile acids. It offers many advantages as regards rapidity of work.

From the analyses of many thousands of samples of butter fat the fact has been deduced that the *Reichert* value is by no means so constant as *Reichert's* researches have led to believe, the quantity of volatile acids being influenced to a notable extent by the seasons, the nature of the food, the period of lactation, the idiosyncrasy of the cow, the method employed in melting the butter, its state of freshness (rancidity), etc.

[1] *Chem. Zeit.* 1892, 1394. The statement made by Bünte (*Chem. Zeit.* 1894, 204) that butter fat is completely hydrolysed by sulphuric acid of specific gravity 1·8355 (corresponding to 93·5 per cent of SO_4H_2) cannot be correct. On repeating Bünte's experiments Thieme (*Proc. K. Akad. Wetensch.* Amsterdam, 1908, 855-860) obtained with sulphuric acid of 93·5 per cent, 98·5 per cent, and 100 per cent SO_4H_2 respectively, products containing in the same order 81·0 per cent, 89·7 per cent, and 92·2 per cent of free fatty acids.

In the following table I have collated the *Reichert-Meissl* (*Reichert-Wollny*) values published by a number of observers, the *Reichert* values (for 2·5 grms.) having been multiplied by 2·2 so as to admit of a comparison with the *Reichert-Meissl* (*Reichert-Wollny*) values, although this procedure is, strictly speaking, not correct. But as the variations in the numbers of different butter fats are greater than the error involved by the employment of a necessarily inaccurate factor, the table will be found sufficiently useful for practical purposes.

Reichert-Meissl (*Reichert-Wollny*) *Values of Butter Fat*

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
English	?	31·9	Muter.
	7	27·6 – 29·2	Vieth.
	7	22·5	Thorpe.
	17	23·5	,,
	15	24·5	,,
	27	25·5	,,
	37	26·5	,,
	357 51	27·5	,,
	78	28·8	,,
	56	29·5	,,
	41	30·5	,,
	18	31·3	,,
	10	32·6	,,
	3	17 – 18·9	van Rijn [1]
	3	19 – 19·9	,,
	8	20 – 20·9	,,
	28	21 – 21·9	,,
Dutch—during September, October, November, December	34	22 – 22·9	,,
	64	23 – 23·9	,,
	428 74	24 – 24·9	,,
	56	25 – 25·9	,,
	67	26 – 26·9	,,
	43	27 – 27·9	,,
	34	28 – 28·9	,,
	9	29 – 29·9	,,
	5	30 – 33	,,
Oct. 17, 1900-Sept. 4, 1901—	632 [2]		
Minimum, in November	...	22·1	van Rijn.
Maximum, in March	.	33·4	,,
Danish (mixed)	7834		
Minimum	.	22·4	Holm and Kvarup.[3]
Maximum	...	33·3	
Swedish	22	26·9 – 29·4	Vieth.
	797	22·9 – 41·0	Nilson.

[1] *On the Composition of Dutch Butter*, London, 1902. Cp. also Reicher, *Zeit. f. ang. Chem.* 1901, 125; Clark, *Analyst*, 1901, 113; *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, London, 1904.

[2] From fifty-three factories.

[3] *Forty-sixth Report of Danish Agricultural Laboratory.* The minimum and maximum values of butters from single cows were 16·8 and 40·0 respectively.

Reichert-Meissl (Reichert-Wollny) Values of Butter Fat—continued

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
Norwegian—			
Nov. 1898 to Dec. 1901—	657 [1]		
Minimum, in June .	...	21·1	
,, in March .	...	28·6	
Maximum, in August .	...	31·2	
,, in January .	...	34·9	
German	?	30·8	Reichert.
	?	27·0 – 31·5	Meissl.
	?	27·6 – 29·4	Reichardt.
	?	24 – 32·8	Sendtner.
	?	22 – 32	Thoerner.
North-West Germany—			
Dec. 1898 to Nov. 1899—			
Minima, in Oct.-Nov. .	...	22·8 – 24·9	Vieth.
Maxima, in April-June	...	29·1 – 31·3	,,
Dec. 1899 to Nov. 1900—			
Minima, in Oct.-Nov. .	...	22·4 – 24·6	,,
Maxima, in April-May	...	29·9 – 31·0	,,
French	?	29·26	Jean.
	28	26·1 – 30·6	Vieth.
	39	26·9 – 30·8	,,
Belgian	693	26 – 36·85	Wauters.
	26	25 – 25·84	,,
	16	24 – 24·96	,,
	9	23·08 – 23·84	,,
	11	19·8 – 23	,,
Italian	178	26·1 – 31·4	Corbetta.
Minima . . .	?	20·63	Spallanzani.
	?	19·8	Spallanzani and Pizzi.
	?	20·68	Vigna.
	?	21·56	Maissen and Rossi.
	?	21·80	Besana.
	?	22·55	Longi.
	?	23·59	Sartori.
Maximum . . .	?	30·14	Spallanzani and Pizzi.
Russian—			
Minimum, in July .	...	25·7	Lewin.
Maximum, in February	...	30·5	,,
October-January . .	161	...	Russian Bacteriological Laboratory
Minimum, in November	...	21·89	,, ,,
Maximum, in January .	...	27·3	,, ,,
Minimum, in April .	74	20·4	St. Petersburg City Laboratory
Maximum, in February	...	30·3	,, ,,

[1] From fifty-three factories.

Reichert-Meissl (Reichert-Wollny) Values of Butter Fat—continued

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer
Finnish—			
January to February	?	30·0–32	Lewkowitsch and Laboratorium für Smörundersökning in Hangö.
March to April	?	29·3–32	
May	?	26·5–31·1	
June to July	...	25·2–30·6	
August	...	24·0–29·1	
September	...	26·4–30·4	
October	...	25·4–30·6	
November	...	27·5–29·9	
December	...	28·7–31·4	
Siberian—			
Minimum	...	24·6	Lewin.
Minimum, in April	150	24·0	Russian Bacteriological Laboratory
Maximum, in August	...	30·7	,, ,,
Swiss	?	28·10–31·10	Ambühl.
American	?	27·36	Cornwall and Wallace.

From the foregoing table it will be gathered that the *Reichert-Meissl* (*Reichert-Wollny*) values of butter fats vary considerably in different countries, and with the different seasons of the year. It appears somewhat unjust to fix a minimum limit (as this may exclude from the market butters produced at certain seasons); still, in order to prevent, to some extent at least, the fraud that would be practised if the *Reichert-Meissl* (*Reichert-Wollny*) value were allowed to fall below a certain number, the minimum value for a genuine butter generally adopted amongst analysts, although not officially, in this country and France is 24, in Germany 25, and in Sweden 23. With regard to the limits fixed by law in Belgium and in Italy compare pp. 678, 679. An enormous amount of evidence has been published [1] to show that under certain conditions—which will be discussed below—the *Reichert-Meissl* value of genuine butter fat may fall, and indeed does fall, below these limits. But it has been also proved that with proper methods of dairying and with proper feeding and stabling, even under severe climatic conditions, the characteristic amount of volatile acids, as expressed by the *Reichert* number, does not vary much, and it would therefore appear unwise to reduce those adopted limits on the strength of individual, mostly exceptional, cases. Such a procedure would undoubtedly lead to greater laxity on the part of the producers of butter. It may be objected, and indeed has been objected, that by fixing a low limit, such as 23, the

[1] Cp. *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

adulterator would be in a position to regulate his admixtures to some extent so as to keep as low a limit as possible. This might perhaps be met by raising the limit, but it should be remembered that the skilled adulterator will in any case adapt himself to given conditions, and especially to the tests applied by those analysts who are likely to examine his butter. At present enormous quantities of butter are sold in this country the fats of which give *Reichert-Meissl* values of exactly 24. Such butters are prepared, almost on a manufacturing scale, by mixing butters rich in volatile fatty acids with margarine, the ingredients being carefully analysed before the admixture takes place.[1] Nor should greater scope be given to what has been aptly termed by *Meissl* "adulteration through the cow" (for such adulteration, see below), caused by bad feeding, or by not stabling the cows when the cold season sets in, or by other conditions which influence the quality of the butter. Dutch butters furnish an instance by which this point may be illustrated. It has been proved[2] that butter made in the northern provinces of Holland during October shows lower *Reichert-Meissl* values than butters produced, on the one hand, in September, and, on the other hand, during November and December. The cause of this decrease in the amount of volatile fatty acids is due to the climatic conditions obtaining during October; after the cows have been stabled in November, the amount of volatile fatty acids again increases.[3]

Several years ago butters imported into the United Kingdom from the north of Holland during these critical months were repeatedly declared by analysts as adulterated, on account of their low *Reichert* values and other abnormalities. It was just this fact which led to the formation of the "Dutch Control Stations." Thus the farmers who produce such butter are now able to prove its purity by affixing the label issued by the Dutch Department of Agriculture (see p. 679). It therefore happens not infrequently that "Dutch Control Butters" with low *Reichert* values are passed as pure, whilst without their labels they would be considered as suspicious and would even be condemned, unless convincing proof as to purity were brought by the vendor.

It cannot be maintained that there exists any connection between the quality of butter and its chemical composition, and a butter need

[1] In this connection a table given by *Wauters* and *Vandam* in a paper, *Sur des cas de falsifications de beurres hollandais importés en Belgique*, will be found instructive. This table shows that butters obtained in Belgium through importing houses exhibit a much more uniform composition, and regularly much lower Reichert values, than butters taken from farms. Their table further shows how carefully the Reichert values are adjusted at the time of official sampling, so that at this time there are hardly any "abnormal" butters in the market.

[2] Van Rijn; Reicher.

[3] The above observation loses in force by the fact that in Mecklenburg the lowest *Reichert-Meissl* values are obtained in the summer months when the cows are out on grass (Vieth, *Chem. Zeit.* 1907, 1231). Hence a more likely reason for the rise of the *Reichert-Meissl* values in Holland after stalling would, in *Vieth's* opinion, appear to be caused by the change in food. But Vieth to some extent contradicts himself by pointing out that his conclusion cannot be taken as applying generally. Cp. also *Paraschtschuk* with regard to Russian butters (*Milchwirthsch. Zentralbl.* 3, 534).

not be of inferior quality because it only contains a low percentage of volatile fatty acids. But even if this point be left an open question, it cannot be denied that to fix the limits too low, or to fix no limit, would be to take out of the hands of the analyst his best weapon against the adulterator and the careless farmer. Since butter from the southern provinces of Holland, where the cows are stabled at nights almost throughout the year, shows no such falling off in the amount of volatile fatty acids, it would follow that the butter manufacturer has it in his power to keep up to a standard which, for want of better analytical methods, may legitimately be considered a just and equitable one.

Similar conditions to those described above obtain in North-West Germany (*Vieth*[1]) and in Siberia;[2] in fact, they can be shown to occur in any country; therefore butter falling below the limit of 24 (*Reichert-Wollny* number) should be considered "abnormal" if further investigation proves that no adulteration with foreign fats has taken place.

The nature of the food also greatly influences the amount of volatile fatty acids. *Spallanzani* and *Pizzi*[3] have shown that when cows are out on grass the butter is rich in volatile acids, which diminish when the cows are stall fed on a *poor* ration.

This agrees with *Swaving's* experience that in the beginning of the grazing season the volatile acids increase, and remain at a high figure until the close of the season.

If cows are fed on oil cakes, the *Reichert-Meissl* value of the fat decreases considerably, in consequence of the oil passing into the milk fat. Thus it has been shown that cows fed with cotton seed cakes yield butter fats of higher melting point (cp. table, p. 671), with a corresponding decrease of about 1 per cent of volatile fatty acids. (It has been mentioned already that butter fat from cows fed with linseed cakes behaves abnormally in the refractometric examination.[4]) *Baumert* and *Falke*[5] especially have shown that on feeding cows with oil cakes, butter fats are obtained which exhibit *Reichert-Meissl* values corresponding to an artificial mixture of butter fat with the oils contained in the cakes.[6] Butters of this kind should at least be looked upon as "abnormal" butters, if not as inferior in quality.

Numerous experiments by other observers have proved that by selecting the food it is possible to alter the composition of the butter fat. Thus cases have occurred in which farmers who fed their cows excessively with cotton cake obtained a butter which would have been condemned, and indeed was condemned at first, as a butter

[1] *Milch Zeitung*, 1901, No. 12.

[2] Cp. *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

[3] *Staz. Sper. Agrar. Ital.* 38, 257.

[4] Cp. Lindsay, *Massachusetts Stat. Rep.* 1900, 14.

[5] Cp. also A. Ruffin, *Ann. de chim. anal.* 1899, iv. 383.

[6] Cp. also A. Burr, *Milch Zeitung*, 1907 (36), 289; 301. Knieriem and Buschmann; v. Knorre and Girgensohn, *Chem. Zentralbl.* 1907, ii. 835, 836.

adulterated with about 30 per cent of oleomargarine. A manufacturer who carries out such admixture by means of dead machinery in a works would certainly be termed an adulterator; and the question may well be raised whether such adulteration "through the cow" may not be made at some future time a punishable offence, just as at present it is not permissible to increase artificially the quantity of milk by giving the cows an excess of salt.

Feeding experiments made with a view to ascertaining the cause of the deficient quantity of volatile soluble acids of the butters in the north of Holland were instituted by *Swaving*.[1] *Van der Zande*, as also *Siegfeld*, have shown that feeding with turnips increases the amount of volatile acids (water-soluble as well as water-insoluble). More recently *Siegfeld*[2] and *Amberger*[3] proved that in this case the insoluble volatile fatty acids increase at a much greater ratio than do the soluble volatile acids (*Reichert-Meissl* value). Since, at the same time, the saponification values rise considerably and the mean molecular weights of the insoluble fatty acids fall in the same ratio, whereas the iodine values become very low, a superficial consideration of the analytical figures might lead to the conclusion that adulteration with cocoa nut oil has taken place were it not for the very high *Reichert-Meissl* values these butters showed, namely, from 31·3 to 32·9. The abnormal production of volatile fatty acids seems to be due to the sugar in the turnips, for *Hoppe-Seyler* has shown, many years ago, that sugar is capable of yielding by purely chemical reactions volatile fatty acids, butyric acid, caprylic acid, etc. Important is also the observation made by *Amberger* that food rich in proteins, such as malt germs, produces the opposite effect, in that the *Reichert-Meissl* values, titration numbers of the insoluble volatile acids, and saponification value fell considerably (in a given case, from 25·5, 1·8, and 225·5 respectively, to 16·7, 1·6, and 219·5), whilst the iodine values rose (from 32·1 to 39·2). Such butter would have been looked upon as adulterated with margarine. The experiments of *Amberger* are all the more convincing, as the feeding experiments, with turnips on the one hand, and with malt germs on the other, were carried out with one and the same set of cows. It is thus possible to produce at will a butter having the characteristics of a butter adulterated with cocoa nut oil or of a butter adulterated with margarine.

Of special importance has become the influence of feeding with cocoa nut cake, for cocoa nut oil passes into the milk fat and alters the chemical composition of the latter. Butters so obtained show high saponification values and low *Reichert-Meissl* values, such as are found in butters adulterated with cocoa nut oil (see below).

Great fluctuations in the composition of butter fat are caused by the **period of lactation.** *Nilson* has shown in the case of Swedish butter that the *Reichert-Meissl* value decreases from 33·44 in the first month to 25·42 in the fourteenth month of lactation. According to

[1] *Zeit. f. Unters. Nahr. u. Genussm.* 1906, ix. 505.
[2] *Ibid.* 1907, xiii. 516. [3] *Ibid.* 1907, xiii. 616.

Vieth, Holstein butter, made at a time when most of the cows were nearing the end of the period of lactation, gave numbers as low as 21·7; also *Spallanzani* and *Pizzi*, and a number of other observers, find higher *Reichert-Meissl* values in the early stages of lactation than in the later ones. [*Swaving*,[1] indeed, went so far as to consider on this account 14 as the permissible minimum.[2]] Similar depressions occur during the rut-time and illness of cows.

As examples of the **idiosyncrasy** of cows may be mentioned experiments carried out by *Einecke*,[3] the object of which was to demonstrate the influence of rape oil, cocoa nut oil, and linseed oil given with the food. Different individuals behaved differently to each kind of oil, and it may be mentioned that, whereas it is accepted that cocoa nut cake stimulates the production of milk and milk fat, *Einecke* found that the influence of cocoa nut oil was rather depressing than stimulating as regards the quantity of fat (see p. 513).

An especially striking example of the idiosyncrasy of cows has been described by *Fischer*.[4] Some butters were suspected on account of their *Reichert* values lying between 16·8 and 19·3. The samples taken in the stable proved that the cows did produce butter fats of such low *Reichert* values as 15·4 and 17·6. Since the food consisted largely of oil cakes (arachis cake, linseed cake, and cotton seed cake), the milk fat of the cows was examined after they had been out on grass for eight days, fourteen days, and five weeks, and the following *Reichert-Meissl* values were found respectively: 17·6, 23·6, and 22·2.

Under the heading of idiosyncrasy may also be considered the influence of the age of the animal on the composition of its milk fat.

Excellent as *Reichert's* method is, sophistication with 20 per cent of a foreign fat in the case of butters rich in volatile acids, or of 10 per cent in the case of butters of ordinary quality, cannot be detected with certainty in every case by the usual rapid methods. Still, *Reichert's* process must be considered the best method hitherto designed for the detection of frauds, or of "abnormal" butters, no other method allowing rapid discrimination between genuine butter and a butter adulterated with a judiciously prepared mixture of margarine and cocoa nut oil. The following table demonstrates this clearly :—

[1] *Landw. Versuchsstat.* 1891, 127.
[2] Cp. also Swaving, *Zeit. f. Unters. Nahr. u. Genussm.* 1905, x. 81 ; 1906, xi. 505.
[3] *Mitt. d. landw. Inst. d. Univ. Breslau*, 1903, 2, 559.
[4] *Zeit. f. Unters. Nahr. Genussm.* 1905, x. 338.

[TABLE

Reichert-Meissl Values

Kind of Fat.	c.c. decinormal Potash.	Observer.
Cocoa nut oil	7·0-7·8	Reichert, Moore, Allen, Muter
Margarine	2·6	Muter
Oleomargarine	0·8-0·9	Jean
Butter fat with 10 per cent of cocoa nut oil .	26·8	,,
,, ,, 20 ,, ,, ,, .	24·13	,,
,, ,, 25 ,, ,, ,, .	24	Muter
,, ,, 50 ,, ,, ,, .	18	,,
,, ,, 75 ,, ,, ,, .	12	,,
50 parts of butter fat, 22·5 parts of cocoa nut oil, and 27·5 parts of oleomargarine . .	17·4	Moore

Only in those cases where margarine free from cocoa nut oil has been used for adulteration, and its proportion exceeds 10 per cent, will the determination of the saponification value prove equally expeditious, since butter fat containing more than 10 per cent of margarine gives a low saponification value (see below). In doubtful cases it is therefore advisable to determine the saponification value as well as the *Reichert* value. Thus, in case butyric acid, butyrin, or amyl acetate have been added to conceal an admixture of margarine, an abnormally high saponification value in conjunction with a normal *Reichert* value will lead to their rapid detection. Furthermore, whenever an abnormally high saponification value is associated with an abnormally low *Reichert* value, the presence of cocoa nut oil may be suspected. In the latter event certainty is obtained by applying the phytosteryl acetate test.

The following table presents several examples of those cases where the *Reichert-Meissl* value just reaches the figure 24, and the analyst is therefore confronted with uncertainty as to whether the butter is adulterated or not :—

No.	Fat.	Reichert-Meissl Value.	Oleo-refracto-meter. Deviation.	Observer.
1	Genuine butter	26-29	−30	Jean
	,, ,, ...	31·9	−34	Muter [1]
2	Cocoa nut oil	7-8	−59	Jean
	,, ,, ...	7·7	−54	Muter
3	Genuine butter with 10 per cent of cocoa nut oil	26·8	−33	Jean
4	,, ,, 15 ,, ,,	...	−34	,,
5	,, ,, 20 ,, ,,	24·13	−36	,,
6	,, ,, 25 ,, ,,	26·4	−39	Muter
7	,, ,, 50 ,, ,,	19·8	−44	,,
8	,, ,, 75 ,, ,,	13·2	−49	,,
9	Margarine	2·8	− 8·5	,,
10	Genuine butter with 25 per cent of margarine	24	−27	,,
11	,, ,, 50 ,, ,,	17·1	−22	,,
12	,, ,, 75 ,, ,,	9·9	−15	,,
13	Margarine with 50 per cent of cocoa nut oil .	6·1	−32	,,
14	50 per cent genuine butter with 25 per cent of margarine and 25 per cent of cocoa nut oil	19·3	−33	,,
15	25 per cent genuine butter with 50 per cent of margarine and 25 per cent of cocoa nut oil	12·3	−27	,,

The specimens represented by Nos. 3 and 4 of the foregoing table cannot be reported as adulterated samples if judged by the *Reichert-Meissl* value and by the refractometric method alone.

The adulterator has taken advantage of this fact, and hence during the last decade—especially in Belgium—large amounts of butter were undoubtedly adulterated with cocoa nut oil.

In cases of this kind, the **phytosteryl acetate test** leads unmistakably to the detection of vegetable oils.

Since this test demands a considerable amount of time, as well as of material, it has been attempted to detect cocoa nut oil in butter fat by a more rapid method, aiming at the determination of the water-insoluble volatile acids.

The Water-insoluble Volatile Fatty Acids

Titration Number of Insoluble Volatile Fatty Acids

The principle underlying the detection of cocoa nut oil by this method rests on the fact that by far the greater part of the volatile fatty acids of *butter fat* obtained in *Reichert's* distillation process is soluble in water, a small quantity only being insoluble, whereas in the case of *cocoa nut oil*, a small amount only of the volatile acids obtained by the *Reichert* distillation process is soluble in water, by far the larger amount being insoluble. By titrating separately these two kinds of fatty acids with decinormal potash, a great difference between butter

[1] The Reichert values given by *Muter* have been multiplied by 2·2 for the sake of better comparison.

fat on the one hand and cocoa nut oil on the other will be observed. This difference can also be traced in butters adulterated with comparatively small quantities of cocoa nut oil (about 10 per cent). This principle was proposed by *Salkowski*[1] and later on has been made use of by *Hart*,[2] *Wauters*,[3] *Vandam*,[4] and *Reychler*.[5] *Wauters* required (on applying his method of distilling twice) 11·4 c.c. of decinormal potash for the soluble volatile acids of cocoa nut oil and 15·4 c.c. for its insoluble volatile acids, whereas several samples of butter fat (taking the mean of three samples) required 27·9 c.c. for the soluble volatile acids and 0·9 c.c. for the insoluble volatile acids.

Although the details of *Wauters'* process have been criticised by *Ranwez*,[6] the underlying principle is a sound one (cp. also *Jean*[7]). It has been carefully worked out almost simultaneously by *Müntz* and *Coudon*[8] in France, and by *Polenske*[9] in Germany, to a new method for determining cocoa nut oil in butter.

In order to obtain constant and comparable results, it is necessary that the minutest details be observed in carrying out the determinations, and it must further be considered as an indispensable condition that the apparatus should conform in every respect to that described by the respective authors.

Müntz and *Coudon* weigh out accurately, with the aid of a finely drawn-out tube, 10 grams of filtered butter fat, melted to a clear liquid, into a cylinder of 5 cm. diameter and 8 cm. height, provided with a spout and tared on an accurate balance. Before the butter commences to solidify, 5 c.c. of a hot concentrated solution of caustic potash are added. The potash solution is prepared by dissolving 120 grams of caustic potash (pure from alcohol), with exclusion of air, in hot water, which is added in small quantities, so that the final volume of the solution, whilst still warm, does not exceed 100 c.c. Should this solution crystallise on cooling, it should be heated on a water-bath until it becomes clear, when small quantities of water are added so that the solution may remain clear at a temperature of 20° C.

With the aid of a glass rod, flattened at the end, the caustic potash is intimately mixed with the butter fat, and the mixing is continued for at least twenty minutes, so as to bring the butter fat particles into intimate contact with the potash. The mass becomes hot at first; when it has become hard, the cylinder is placed in an oven heated to 70-80° C., and left therein for twenty minutes; this is sufficient to effect complete saponification. With the aid of the glass rod, the hard soap is broken up and reduced to a coarse powder. This is then transferred with the aid of 200 c.c. of distilled water, accurately measured off, into a distilling flask. The flask is gently

[1] *Zeit. analyt. Chem.* 1887, xxvi. 582. [2] *Chem. Zeit.* 1901, 207.
[3] *Bull. de l'Assoc. Belge de Chim.* 1901, 258.
[4] *Ann. de pharm. de Louvain*, 1901, 201. For a criticism of Vandam's method, cp. Fendler (*Arbeit. a. d. pharm. Inst. d. Univ. Berlin*, 1908).
[5] *Bull. de la Soc. Chim.* 1901, 142.
[6] *Ann. Pharm.* 1901, 241. Cp. Van Leent, *Chem. Zentralblatt*, 1903, ii. 1193.
[7] *Annal. chim. anal. appl.* 1903, 441.
[8] *Annales de l'Institut national agronomique* [3] (2), 1904, Fasc. 1.
[9] *Arbeit. aus dem kaiserl. Gesundheitsamte*, 1904, 545.

heated over a Bunsen burner with frequent shaking, care being taken that no loss of water occurs through evaporation. When the soap is dissolved completely and cooled down to the ordinary temperature, 30 c.c. of a phosphoric acid solution of 1·15 specific gravity are added. (This solution is prepared by dissolving syrupy phosphoric acid of 45° Bé in about twice its volume of water.) Finally, a few pieces of pumice stone are introduced.

The carbonic acid which is combined with the potash would render the determination incorrect; in order to remove it, the flask is connected with a vacuum pump and exhausted for ten to fifteen minutes while the cold acid solution is carefully shaken. The dis-

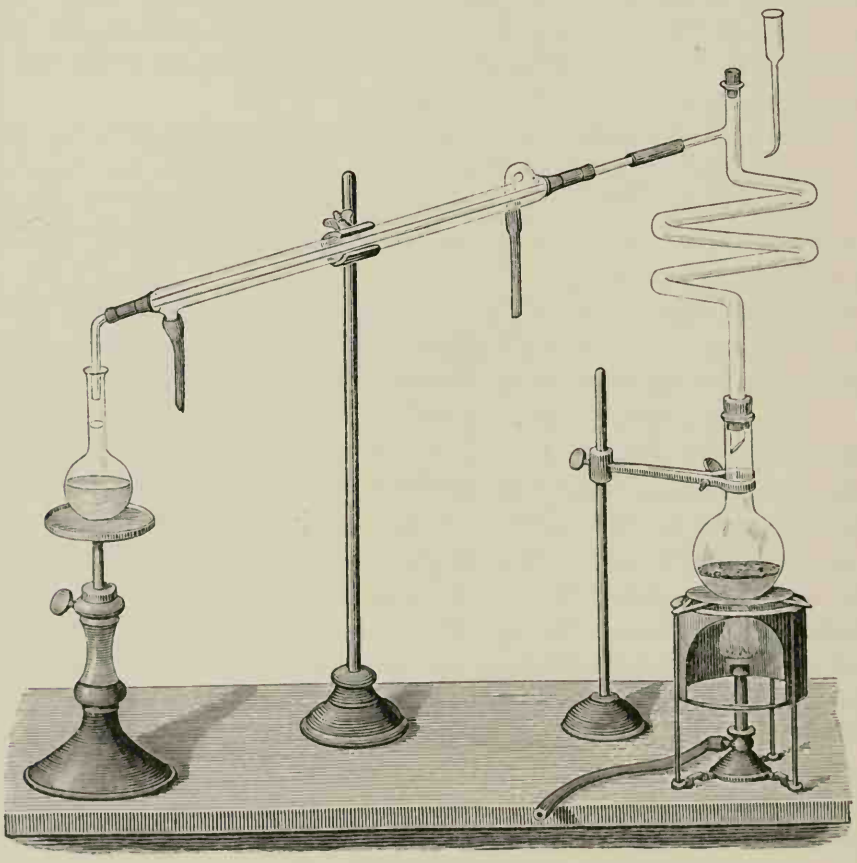

Fig. 15.

tilling flask is fitted with a dephlegmator and is connected with a condenser exactly as shown in the figure. The distilling flask is of Bohemian glass, and holds 500 c.c. up to the commencement of the neck; the latter is 9 cm. long and has a diameter of 20 mm. The dephlegmator is made from a glass tube 1 metre long, having an outside diameter of 16 mm. and inside diameter of 14 mm. It is bent exactly as is shown in the illustration. The lower end is cut off aslant; a side tube is sealed into the upper end. The upper end of the dephlegmator is closed by an india-rubber stopper. The dephlegmator has a vertical height of 35 cm.; about 92 cm. of the total length of the tube thus serve for cooling the vapours.

The flask is heated direct over a Bunsen burner; in order to avoid overheating of the sides, especially towards the end of the distillation, the flask is placed on a copper ring of 13 cm. diameter, having a hole 6 cm. in diameter. The flame is so regulated that the distillation lasts about one hour and a half. The distillate is received in a 200 c.c. graduated flask. The distillation is interrupted when exactly 200 c.c. have distilled over.

The liquid in the measured flask is more or less turbid, and on its surface there float oily drops of insoluble volatile acids. In order to facilitate the separation of the insoluble volatile acids from the soluble volatile acids, the liquid is allowed to stand till the following day, and is then filtered through a moistened filter paper. The insoluble acids remain on the filter and the soluble acids are collected in a 750 c.c. beaker. The flask is washed with 5 c.c. of water, which are also thrown on the filter.

All these precautions are indispensable in order to obtain a good separation of the soluble from the insoluble volatile acids, as otherwise, *e.g.*, if the time allowed for separation were shortened, small quantities of insoluble acids would pass through the filter, which would be indicated by the turbid appearance of the filtered liquid. In order to obtain constant results, it is indispensable that the aqueous solution should be perfectly clear. To the clear filtrate six drops of a 1 per cent solution of phenolphthalein are added and the liquid titrated with standardised lime water. 100 c.c. of the lime water are run in at once from a pipette, and the titration is then completed with the same standard lime solution, added from a burette. The titration is finished when the pink colour persists in the liquid for a few seconds. The number of c.c. of lime solution used for titration is calculated to butyric acid.

The insoluble volatile acids which have remained to the largest extent on the filter, and traces of which still adhere to the 200 c.c. flask, as also to the cooling tube of the condenser, are collected by placing the filter on the 200 c.c. flask and treating it with four successive washes of alcohol of 5 c.c. each, allowing the alcohol to fall drop by drop from a pipette on to the filter. The 200 c.c. flask is then placed under the condenser, the outlet of which has meanwhile been closed by means of an india-rubber tube and pinch-cock. The condenser is detached from the dephlegmator, and about 200 c.c. of alcohol are run into the cooling tube of the condenser through a small funnel. The alcohol is allowed to remain for some minutes in the tube and is then run into the 200 c.c. flask by opening the pinch-cock. The condenser tube is washed once more with 5-6 c.c. of alcohol. The alcohol must be neutral, and be of 95° (*Gay Lussac*?). The insoluble volatile acids, which are now completely collected in the 200 c.c. flask, are titrated (after addition of four drops of phenolphthalein solution) with standard lime solution, which is allowed to run in from a burette. The quantity of volatile insoluble acids is also expressed in terms of butyric acid.

It will be seen that *Müntz* and *Coudon* deviate from the *French*

official method (described Vol. I. Chap. VIII.) in the determination of the volatile acids, and approach the method of *Reichert-Meissl* with this important difference that they employ double the quantity of material and collect twice the volume of distillate. I append, in the following table, the results obtained by *Müntz* and *Coudon* in the examination of forty butters obtained from different departments of France :—

No.	Soluble Volatile Acids.	Insoluble Volatile Acids.	Relation (Rapport).
	In Terms of Butyric Acid.		$\frac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100.$
	Per cent.	Per cent.	
1	5·55	0·57	10·3
2	6·01	0·77	12·8
3	6·00	0·75	12·5
4	5·10	0·50	9·9
5	5·14	0·73	14·2
6	5·52	0·63	11·4
7	5·62	0·69	12·3
8	5·72	0·52	9·1
9	5·50	0·65	11·8
10	5·38	0·50	9·2
11	5·24	0·50	11·4
12	5·94	0·63	10·5
13	5·73	0·66	11·6
14	5·54	0·79	14·3
15	5·70	0·87	15·1
16	5·86	0·61	10·5
17	5·52	0·61	11·0
18	5·61	0·79	14·2
19	5·44	0·75	13·7
20	5·55	0·68	12·2
21	5·24	0·71	13·5
22	5·70	0·69	12·1
23	5·19	0·59	11·3
24	4·83	0·67	13·8
25	4·79	0·68	14·1
26	5·61	0·60	10·7
27	5·47	0·72	13·2
28	5·24	0·55	10·5
29	5·45	0·64	11·8
30	5·19	0·81	15·6
31	5·02	0·59	11·7
32	5·47	0·54	9·8
33	5·07	0·58	11·4
34	5·26	0·68	12·9
35	5·14	0·71	13·8
36	5·18	0·69	13·3
37	5·01	0·59	11·8
38	5·01	0·64	12·7
39	5·43	0·51	9·3
40	5·20	0·54	10·3
		Average 0·652	12·04
		Minimum 0·50	9·1
		Maximum 0·87	15·6

On referring to p. 519 it will be gathered that the relation :— insoluble volatile acids ÷ soluble volatile acids × 100 varies for cocoa nut oil between the numbers 250·3 and 314·7. The enormous difference which exists in this respect between butter fat and cocoa nut oil permits the recognition of an admixture of cocoa nut oil to butter. This is confirmed by the following table, in which I have collated a number of figures published by *Müntz* and *Coudon* :—

	Soluble Volatile Acids.	Insoluble Volatile Acids.	Relation.
	In Terms of Butyric Acid.		$\frac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100.$
	Per cent.	Per cent.	
Mixtures of Pure Butter with 20 *per cent Cocoa Nut Oil, No.* 1 (p. 519)			
1. Pure butter (Sarthe) . . .	5·67	0·71	12·5
Do. containing 20 per cent cocoa nut oil . .	4·82	1·31	27·2
2. Pure butter (Normandy) . .	5·88	0·62	10·6
Do. containing 20 per cent cocoa nut oil . .	5·09	1·28	25·0
3. Pure butter (Bretagne) . .	5·56	0·56	10·0
Do. containing 20 per cent cocoa nut oil . .	4·81	1·40	29·0
Mixtures of Pure Butter with 15 *per cent Cocoa Nut Oil, No.* 1 (p. 519)			
1. Pure butter (Seine Inférieure) .	5·34	0·69	12·9
Do. containing 15 per cent cocoa nut oil . .	4·71	1·19	25·2
2. Pure butter (Sarthe) . . .	5·67	0·71	12·5
Do. containing 15 per cent cocoa nut oil . .	5·03	1·10	21·9
3. Pure butter (Finistère) . .	5·52	0·63	11·4
Do. containing 15 per cent cocoa nut oil . .	4·71	1·11	23·6
Mixtures of Pure Butter with 12·5 *per cent Cocoa Nut Oil, No.* 1 (p. 519)			
1. Pure butter (Vendée) . . .	5·71	0·73	12·8
Do. containing 12·5 per cent cocoa nut oil .	5·20	1·16	22·4
2. Pure butter (Charente-Inférieure)	5·24	0·71	13·5
Do. containing 12·5 per cent cocoa nut oil .	5·19	1·08	20·7
3. Pure butter (Charente-Inférieure)	5·44	0·75	13·7
Do. containing 12·5 per cent cocoa nut oil .	4·84	1·23	25·3

[TABLE

Mixtures of Pure Butter with 10 *per cent Cocoa Nut Oil, No.* 2 (p. 519)

	Soluble Volatile Acids.	Insoluble Volatile Acids.	Relation.
	In Terms of Butyric Acid.		$\frac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100$.
	Per cent.	Per cent.	
1. Pure butter (Seine Inférieure) .	5·34	0·69	12·9
Do. containing 10 per cent cocoa nut oil .	4·90	1·01	20·6
2. Pure butter (Morbihan) . .	5·56	0·56	10·0
Do. containing 10 per cent cocoa nut oil .	5·23	1·03	19·6
3. Pure butter (Vendée) . . .	5·73	0·66	11·6
Do. containing 10 per cent cocoa nut oil .	5·30	1·02	19·2

Exactly the same principle underlies the method of *Polenske*, who works with 5 grams of butter fat, and adapts himself more completely to the *Reichert-Meissl* (*Wollny*) method than *Müntz* and *Coudon* did.

Polenske saponifies 5 grms. of filtered butter fat, by the *Leffmann-Beam* process, with 20 grms. of glycerin and 2 c.c. of caustic soda solution (prepared from equal parts of sodium hydrate and water) in a 300 c.c. flask by heating over a free flame. The solution is allowed to cool below 100° C., 90 c.c. of water are added, and the mass dissolved by warming on the water-bath to about 50° C. The solution must be clear and almost colourless. In case a brown solution be obtained, the test must be rejected. 50 c.c. of dilute sulphuric acid (containing 25 c.c. of pure concentrated sulphuric acid in 1000 c.c.) and some *powdered* pumice are added to the hot soap solution ; the flask is then immediately attached to the condenser. The apparatus to be employed must correspond in all details to the dimensions given in Fig. 16. The heat must be so regulated that within nineteen to twenty minutes 110 c.c. are distilled off; the cooling water must be supplied at such a rate that the distillate does not drop into the 110 c.c. flask at a higher temperature than 20°-23° C. As soon as 110 c.c. have distilled over, the distillation is interrupted, the flask is removed, and is replaced by a 20 c.c. measuring cylinder.

The distillate, which must not be shaken through, is immersed almost completely in water of 15° C. After about five minutes the neck of the flask is slightly tapped so that the oily drops floating on the surface may adhere to the walls of the flask. After a further ten minutes the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a solid (semi-solid) mass or oily drops. The contents of the flask are then mixed by turning

the corked flask four or five times upside down, avoiding, however, violent shaking. 100 c.c. are filtered off through a filter of 8 cm. diameter, and titrated with decinormal caustic potash, as is done in the determination of the *Reichert-Meissl* value. In order to remove the soluble acids completely, the insoluble volatile acids on the filter are washed three times in succession with 15 c.c. of water, which have been passed severally through the tube of the condenser, the 20 c.c. measuring cylinder, and the 110 c.c. flask. These wash-waters are thrown away. In order to collect the insoluble volatile acids adhering to the tube of the condenser, the measuring cylinder, and the 110 c.c. flask, these vessels are rinsed three times in succession with 15 c.c. of neutralised 90 per cent alcohol, and the alcoholic washes poured through the filter, each quantity being allowed to drain before a fresh wash is poured on the filter. The alcoholic filtrate is then titrated with decinormal alkali.

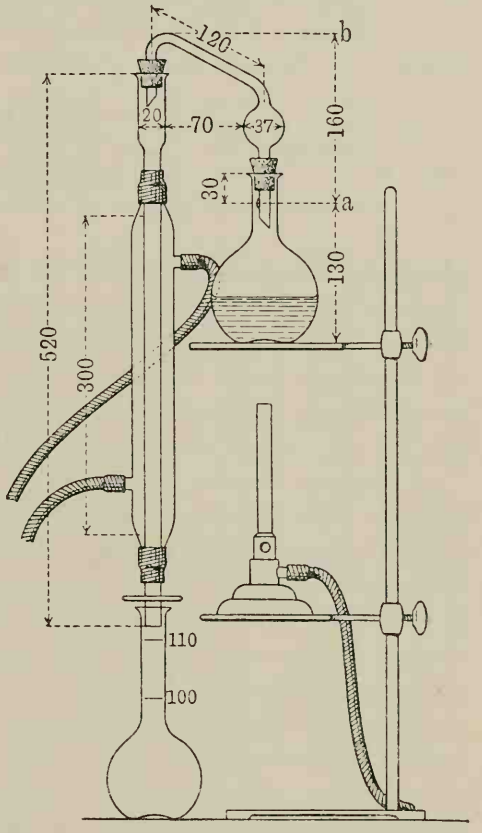

Fig. 16.

Polenske ascertained, by examining thirty-four samples of butter fat, the *Reichert-Meissl* values of which varied from 23·3 to 30·1, that the amount of decinormal alkali required for the insoluble volatile fatty acids varied from 1·5 to 3·0 c.c., whereas in the case of four samples of cocoa nut oil having the *Reichert-Meissl* values 6·8 to 7·7, as much as 16·8 to 17·8 c.c. of decinormal potash were required for the neutralisation of the insoluble volatile acids. (The number of c.c. of decinormal alkali required for the neutralisation of the *insoluble* volatile fatty acids is termed by *Polenske* "new butter value.") *Polenske* further lays stress on the fact that the insoluble volatile fatty acids of butter fat form oily drops, if the *Reichert-Meissl* value of the butter fat be low, or a semi-solid, non-transparent mass in case the *Reichert-Meissl* value be high. He further observed that if 10 or more per cent of cocoa nut oil be admixed to butter fat, the insoluble volatile acids no longer solidify. (This is explained by *Polenske* by the fact that the volatile acids of cocoa nut oil contain large quantities of caprylic acid, whereas in the case of butter fat capric acid predominates.)

Polenske's method is in its first stage almost identical with the *Reichert* method. A large number of experiments have demonstrated

that it is absolutely necessary to follow the process in all its minutest details, in order to obtain concordant results.

In the following table I reproduce a number of values published by *Polenske* for pure butter fats, and for the same butter fats after they have been admixed with 10 per cent, 15 per cent, and 20 per cent of cocoa nut oil respectively :—

No.	Number of c.c. $\frac{1}{10}$ norm. KOH, "Titration Numbers," required for the Neutralisation of the							
	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids.
	of Pure Butter Fat.		of Same Butter Fat containing 10 per cent of Cocoa Nut Oil.		of Same Butter Fat containing 15 per cent of Cocoa Nut Oil.		of Same Butter Fat containing 20 per cent of Cocoa Nut Oil.	
1	19·9	1·35	18·7	2·4	18·1	2·9	17·6	3·3
2	21·1	1·4	19·7	2·3	19·2	3·0	18·5	3·6
3	22·5	1·5	21·0	2·5	20·4	2·9	19·8	3·5
4	23·3	1·6	22·0	2·5	21·5	3·1	21·0	3·7
5	23·4	1·5	22·3	2·4	21·7	3·1	21·2	3·7
6	23·6	1·7	22·5	2·5	21·9	3·3	21·4	4·0
7	24·5	1·6	23·3	2·5	22·4	3·1	21·7	3·7
8	24·7	1·7	23·8	2·9	22·9	3·5	22·1	3·9
9	24·8	1·7	23·5	2·7	22·7	3·2	...	...
10	24·8	1·6	23·4	2·5	22·8	3·0	22·1	3·6
11	25·0	1·8	23·0	2·7	23·3	3·1	21·8	3·6
12	25·1	1·6	23·5	2·5	23·1	3·0	22·5	3·8
13	25·2	1·6	23·4	2·6	22·9	3·0	22·3	3·7
14	25·3	1·8	24·0	2·9	23·5	3·5	22·6	4·1
15	25·4	1·9	24·2	3·0	23·7	3·6	22·6	4·1
16	25·6	1·7	24·1	2·7	23·3	3·1	22·7	3·7
17	25·4	1·7	23·8	2·6	23·0	3·1	...	...
18	26·2	1·9	25·0	3·1	24·2	3·6	23·6	4·0
19	26·5	1·9	25·0	2·9	24·1	3·5	23·2	4·1
20	26·6	1·8	25·4	2·9	24·6	3·3	23·9	3·8
21	26·7	2·0	25·2	3·2	24·5	3·6	23·7	4·2
22	26·8	2·0	24·8	3·0	24·2	3·4	23·5	4·0
23	26·9	2·1	25·2	2·9	24·1	3·6	23·2	4·2
24	26·9	1·9	24·9	2·9	24·0	3·3	23·3	4·0
25	27·5	1·9	25·7	2·7	24·9	3·3	24·0	3·9
26	27·8	2·2	26·0	3·1	25·0	3·7	...	...
27	28·2	2·3	26·1	3·1	25·1	3·8	24·5	4·4
28	28·4	2·3	26·5	3·5	25·7	4·0	25·1	4·5
29	28·8	2·2	26·8	3·3	26·0	3·9	...	...
30	28·8	2·5	27·1	3·5	26·3	4·0	25·4	4·7
31	29·4	2·6	27·6	3·8	26·9	4·2	...	...
32	29·6	2·8	27·5	3·8	26·2	4·2	25·5	4·9
33	29·5	2·5	27·4	3·5	26·6	4·1	25·4	4·7
34	30·1	3·0	27·8	3·8	26·9	4·4	26·2	5·0

With the assistance of this table *Polenske* claimed to be able to calculate quantitatively (though only approximately) the admixed cocoa nut oil in an adulterated butter fat, relying on the conclusion

derived from the thirty-four given samples, viz. that the amount of alkali required for the neutralisation of the insoluble volatile acids is increased by 0·1 c.c., through the addition of 1 per cent of cocoa nut oil. An example may illustrate his manner of calculation :— A sample of butter fat gave the *Reichert-Meissl* value 24·5, and required for the neutralisation of the insoluble volatile fatty acids 3·0 c.c. of decinormal alkali. The insoluble volatile acids were found to be liquid. According to the foregoing table, a *pure* butter fat of the *Reichert-Meissl* value 24·5 requires only 1·6 c.c. of decinormal alkali for the neutralisation of the insoluble volatile acids ; hence, there was used an excess of $3{\cdot}0 - 1{\cdot}6 = 1{\cdot}4$ c.c. for the neutralisation of the insoluble volatile fatty acids. The sample must therefore be judged to have been adulterated with cocoa nut oil. Since each 0·1 c.c. is taken to correspond to 1 per cent of added cocoa nut oil, the sample would contain 14 per cent of cocoa nut oil. Examples 15 and 22 of the foregoing table (24·2 ; 3·0 and 24·8 ; 3·0) would point to an admixture of 10 per cent of cocoa nut oil. The sample which gave these numbers actually did contain 10 per cent of cocoa nut oil.

Although these methods must be considered as valuable additions to the armoury of the analytical chemist, the fact should not be overlooked that some uncertainty adheres to them, especially as regards the quantitative interpretation, since the value of these methods can be rendered nugatory by the employment of smaller quantities of cocoa nut oil than 10 per cent, or of a mixture of cocoa nut oil and margarine or of edible palm kernel oil instead of cocoa nut oil.

Unfortunately the results obtained by the two methods are not comparable, and it must, therefore, be repeated once more that it is necessary to adhere strictly to the working conditions laid down by *Müntz* and *Coudon* on the one hand and by *Polenske* on the other if it be desired to institute a comparison with the above given figures. Moreover, it must not be overlooked that in the examples given above the composition of both the original butter and the admixed cocoa nut oil were known. This is, of course, not the case if a commercial sample be under examination. Whereas the composition of cocoa nut oil does not fluctuate within wide limits (see, however, below), the vagaries of butter fat may, in case only small additions of cocoa nut oil have been made, entirely nullify the indications to be drawn from the above given tables.

Polenske in his original communication gave a table setting out the maximum permissible titration numbers for the insoluble volatile acids of butter fats corresponding to all *Reichert-Meissl* values lying between 20 and 30. I have not reproduced this table, as in my own experience with different butter fats examined by *Polenske's* method, I found that the assumed regularity which he had derived from his figures did not hold good for my specimens. Thus, whereas *Polenske* gave the titration numbers for the insoluble volatile acids of butter fats having *Reichert-Meissl* values from 29 to 30 as 2·5-3·0, with the maximum permissible limit of 3·5, I have obtained the

following figures with a number of undoubtedly pure French and Finnish butters :—

Titration Numbers of Soluble and Insoluble Volatile Acids (Lewkowitsch)

Soluble Volatile Acids R.-M. Value.	Insoluble Volatile Acids.
29·3	3·29
29·31	3·19
29·32	2·53
29·37	2·80
29·96	2·24
30·02	3·27
30·15	3·24
30·49	3·50
31·0	3·06
31·41	4·1
31·49	3·6
31·99	3·03

It must be conceded that in the face of these numbers no fixed rule as to maximum permissible numbers, and consequently as to the presence of cocoa nut oil in the case of an unknown sample, can be derived from the titration numbers of the insoluble volatile acids. It should further be added that the limits given by *Polenske* for the insoluble volatile acids of cocoa nut oil cannot be accepted as having general applicability, for I have found for a number of edible cocoa nut oils of the *Reichert-Meissl* values 7·32 to 7·5, titration numbers of the insoluble volatile acids lying between 15·49 and 20·45. Furthermore, it should be noted that if palm kernel oil instead of cocoa nut oil be admixed with butter fat much smaller titration numbers will be found for the insoluble volatile acids, since palm kernel oil yields, in *Polenske's* test, numbers lying between 10 and 12.

Whereas the method proposed by *Müntz* and *Coudon* has not been made the subject of further publications, a large number of observers have repeated *Polenske's* experiments, and have confirmed the strictures I have expressed above. Amongst those observers are *Hesse*,[1] *Wiedmann*,[2] *Arnold*,[3] *Farnsteiner*,[4] *O. Jensen*,[5] *Lührig*,[6] *Siegfeld*,[7] *Kühn*,[8] *Rideal* and *Harrison*,[9] *Thorp*,[10] *Kühn*,[11] and *Fritzsche*.[12] *Siegfeld* has published a considerable number of analyses of genuine butters, and has shown that the generalisation expressed by *Polenske's* additional table (omitted in this work) does not hold good, that wide deviations therefrom must be allowed, and that the titration numbers of the insoluble volatile acids are subject to the same fluctuations as the *Reichert-Meissl* values.

[1] *Milchwirthsch. Zentralblatt*, 1905, i. 13.
[2] *Molkerei Zeitung Hildesheim*, 1904, **18**, 29.
[3] *Zeit. f. Unters. Nahr. u. Genussm.* 1905, x. 202.
[4] *Ibid.* 1905, x. 51.
[5] *Ibid.* 1905, x. 276.
[6] *Ibid.* 1906, xi. 14.
[7] *Milchwirthsch. Zentralblatt*, 1906, Heft 4, 289 ; Heft 7, 145.
[8] *Ibid.* 1907, xiv. 741.
[9] *Analyst*, 1906, 256.
[10] *Ibid.* 1906, 357.
[11] *Zeit. f. Unters. Nahr. u. Genussm.* 1907, xiv. 743.
[12] *Ibid.* 1908, xv. 193.

Nay, it has even been demonstrated that through the vagaries of butter fat the titration numbers of the insoluble volatile acids are liable to greater fluctuations than the *Reichert-Meissl* numbers themselves.

Nor have more recent observations confirmed *Polenske's* statement that the insoluble volatile acids of butter fat no longer solidify in case 10 per cent or more of cocoa nut oil have been admixed with the butter. For I have frequently observed that genuine butters with high *Reichert-Meissl* values yielded insoluble volatile acids, which did not solidify at 15° C.

It must, therefore, be concluded that the results obtained in the determination of the insoluble volatile acids by either method must be looked upon with great circumspection, and that *no definite conclusions* can be drawn, unless they are supported by other evidence—chiefly the **phytosteryl acetate test** (see below).

It should be remembered that when cows are fed with cocoa nut cake their milk fat simulates, in its chemical composition, a butter fat to which small quantities of cocoa nut oil have been admixed, in that it exhibits a low *Reichert* value and a high saponification value, and also a high titration number of the insoluble volatile fatty acids. This pitfall should at present be especially guarded against, as in consequence of the enormous expansion of the edible cocoa nut oil industry very large quantities of cocoa nut cake are given to milch cows (see p. 513). Though butters obtained from cows so fed are genuine, they may raise grave suspicions in the mind of the analyst when "abnormal" figures are obtained.

To give an example, *Juckenack* and *Pasternack*[1] have published the following analyses of two genuine butter fats, which were looked upon as extremely suspicious on account of the analytical data which they furnished :—

	Butter No. 1.	Butter No. 2.
Saponification value	236·95	235·80
Reichert-Meissl value	27·05	27·15
Titration number of insoluble volatile acids .	3·50	2·40
Mean Molecular Weight of the insoluble fatty acids	253·05	252·45

It should further be borne in mind that feeding with turnips, or turnip leaves, increases the titration numbers of the insoluble volatile fatty acids in a much higher degree than the titration numbers of the soluble volatile fatty acids (*Reichert-Meissl* values), so that also through this cause unjustified suspicion may be raised against butters in which the proportion of insoluble volatile to soluble volatile acids deviates considerably from the figures quoted above.

In such cases it is absolutely indispensable to have recourse to the **phytosteryl acetate test**, as this leads unmistakably to the detection of cocoa nut oil, for it has been pointed out (p. 544) that numerous experiments have demonstrated that any phytosterol given with the food does not pass into the milk fat. Therefore it is easy to distinguish butter fats to which cocoa nut oil has been added

[1] *Zeit. f. Unters. Nahr. Genussm.* 1906, xi. 159.

fraudulently from those butter fats which simulate adulterated specimens through the fact that the milch cows have been fed with cocoa nut cake. Since the phytosteryl acetate test reveals the smallest quantities of vegetable fat present, it is possible by this means to detect with certainty 10 per cent (and even less) of fraudulently added cocoa nut oil.

In order to prove this by actual experiments I prepared mixtures of pure butter with 10 per cent of cocoa nut oils, containing 0·23 per cent and 0·179 per cent respectively of unsaponifiable matter. In the following table the results of this examination are tabulated :—

Phytosteryl Acetate Test with pure Butter Fat, pure Cocoa Nut Oil, and with a Mixture containing 10 *per cent of Cocoa Nut Oil (Lewkowitsch)*

	Pure Butter Fat. ° C.	Pure Cocoa Nut Oil. ° C.	Mixture of pure Butter Fat with 10 per cent of Cocoa Nut Oil, yielding Unsaponifiable Matter.	
			0·23 per cent.	0·179 per cent.
Melting point of 2nd crop of crystals .	112	129-130	115-117	113·5
Do. 5th do.	113·5	...	123-124	123·0
Do. 7th do.	113·5	...	...	...

It should not be forgotten that the information furnished by the phytosteryl acetate test, as carried out ordinarily, may be rendered nugatory by the fraudulent addition of a small amount of paraffin wax to the butter fat. It has been shown above ("Lard," p. 592) how the paraffin wax can be eliminated, so that the indications of the phytosteryl acetate test become absolutely reliable.

I wish to emphasise again that, if serious errors are to be avoided, in each doubtful case the indications of the insoluble volatile acid test must be supplemented by the phytosteryl acetate test.

Altogether futile must be judged the attempt of some analysts to derive the conclusion that an admixture of beef fat or lard has taken place if only low titration numbers for the insoluble volatile acids are found. This erroneous conclusion had indeed been propounded within the author's experience in the case of a number of butter fats having *Reichert-Meissl* values of about 25·6 to 26·2, and titration numbers (for the insoluble volatile acids) 2·01 to 2·06, because the additional table published by *Polenske* (omitted here for the reasons stated above) indicated that the titration number should be 2·4. It need hardly be pointed out that conclusions resting on such slavish adherence to figures derived from too small a number of

observations on butters produced within a limited area, are entirely devoid of general applicability. Emphasis should be laid on this, since it may happen that a miscarriage of justice may follow, especially if, on the strength of such erroneous conclusions, the amount of supposed beef fat or lard be calculated with the help of the "rule of three."

The presence of cocoa nut oil in butter fat can also be detected by resolving the suspected butter fat into two fractions, with 95 per cent alcohol (in the manner described under "Lard," p. 572), and examining each fraction separately. This is illustrated by the following table due to *Arnold*[1]:—

[1] *Zeit. f. Unters. d. Nahr. u. Genussm.* 1907, xiv. 195. Cp. also table, p. 675, for pure butter fat.

[TABLE

Butter Fat containing 6 *per cent Cocoa Nut Oil*

	Butyro-refracto-meter at 40° C. "Degrees.'	Saponifica-tion Value.	Reichert-Meissl Value.	Mean Molecular Weight of the Soluble Volatile Acids.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids (Polenske's Method).	Iodine Value.	Non-volatile Fatty Acids.			150 Grms. of Fat yielded Alcohol-soluble Portion.
							Butyro-refracto-meter at 40° C. "Degrees."	Neutralisa-tion Value.	Iodine Value.	
										Grms.
I. Original Fat . . .	43·1	226·2	23·4	103·0	2·65	40·0	31·3	219·8	43·6	...
II. Alcohol-soluble Fat . .	40·6	235·2	34·6	102·5	3·8	41·2	32·6	219·0	46 0	35·59
III. Alcohol-insoluble Fat .	44·05	221·8	20·3	107·0	2·2	39·5	31·3	218·2	40·4	...

In conclusion, it should be pointed out that the determination of the titration number of the insoluble volatile acids is usefully supplemented by the *phytosteryl acetate test*, which in its present form does not admit of quantitative interpretation, and which obviously becomes useless in case a margarine "ear-marked" with sesamé oil or containing other vegetable oils and fats has been employed as an adulterant.

As a qualitative test, capable of indicating 5 per cent or 10 per cent of cocoa nut oil in butter fat, *Hinks*[1] recommends the following method: 5 c.c. of the melted and filtered fat are dissolved in 10 c.c. of ether in a test tube, which is then corked up and placed in ice. In the course of half an hour a certain amount of solid glycerides will be found to have separated out, leaving a clear ethereal solution as an upper layer. The ether is poured on a filter, and filtered rapidly. The ethereal solution is evaporated down on the water-bath, the residual fat brought into a test tube and boiled with three to four times its volume of 96-97 per cent alcohol, in order to effect complete solution. On allowing the solution to cool to the ordinary temperature, most of the fat separates. The tube is placed next in water at 5° C., and kept at that temperature for fifteen minutes. The alcoholic layer is then rapidly filtered into another test tube, which is placed in ice, and kept at 0° C. for two or three hours. A flocculent deposit soon separates out. A portion having been withdrawn by the aid of a wide-mouthed pipette and placed on a slide, the crystals are examined microscopically under a magnification of 250-300, care being taken that the crystals are not broken by pressing the cover on the slide.

The glycerides deposited from pure butter fat form round granular masses, whereas cocoa nut oil yields fine needle-shaped crystals, the forms of which can be readily observed even at a lower power than 250. In the case of a mixture of cocoa nut oil and butter fat, the deposit shows granular butter fat spheres side by side with numerous small, very fine, almost feathery crystals. These will generally be found attached to the butter fat granules, but sometimes they form clusters by themselves, their characteristic appearance being that of a mass of crystals growing from the side of the butter granules. *Hinks* states that the presence of 10 per cent of beef fat, cotton seed oil, or sesamé oil does not mask the presence of cocoa nut oil. Lard, however, does interfere with this test, inasmuch as, treated by this process, lard yields stellate clusters of crystals which almost completely suppress the granular appearance of the butter fat crystals.

It should be noted that alcohol of less strength than 95 per cent is inadmissible, since butter fat has the tendency to assume crystalline form on separating from weaker alcohol. As the deposit is soluble in alcohol at the ordinary temperature, or at any rate loses its crystalline form, the microscopical examination must be conducted rapidly. If the temperature of the room should be somewhat high, the slide must be kept cool on a shallow glass dish containing clear

[1] *Analyst*, 1907, 160.

lumps of ice. *Hinks* concludes from several experiments that the feeding of cows with cocoa nut cake does not interfere with this test.[1]

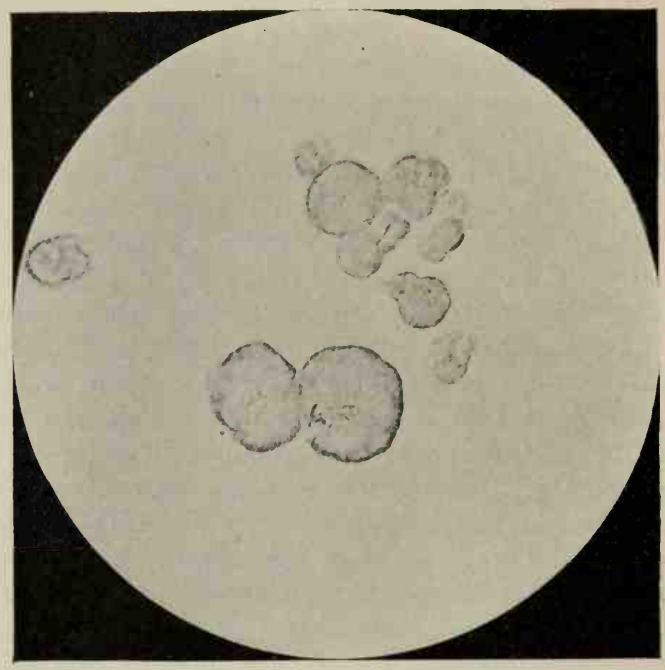

Fig. 17.—Pure Butter. 200 diam.

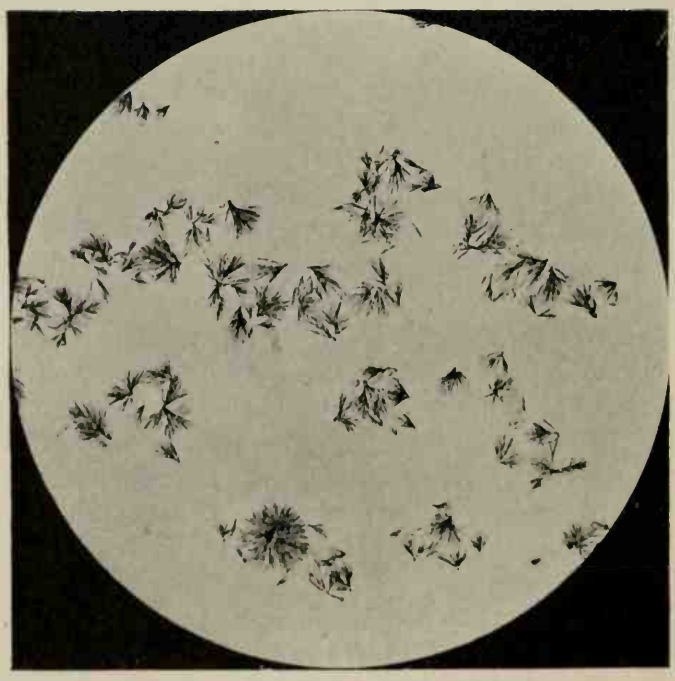

Fig. 18.—Pure Cocoa Nut Oil. 70 diam.

Further indications are furnished by the microscopical slides reproduced here.[2]

[1] Cp., however, Lahache, *Journ. Pharm. Chemie*, 1903 (18), 338.

[2] These photomicrographs were prepared by E. R. Bolton.

A considerable number of other methods aiming at the detection of cocoa nut oil in butter fat are omitted here, for the reason that

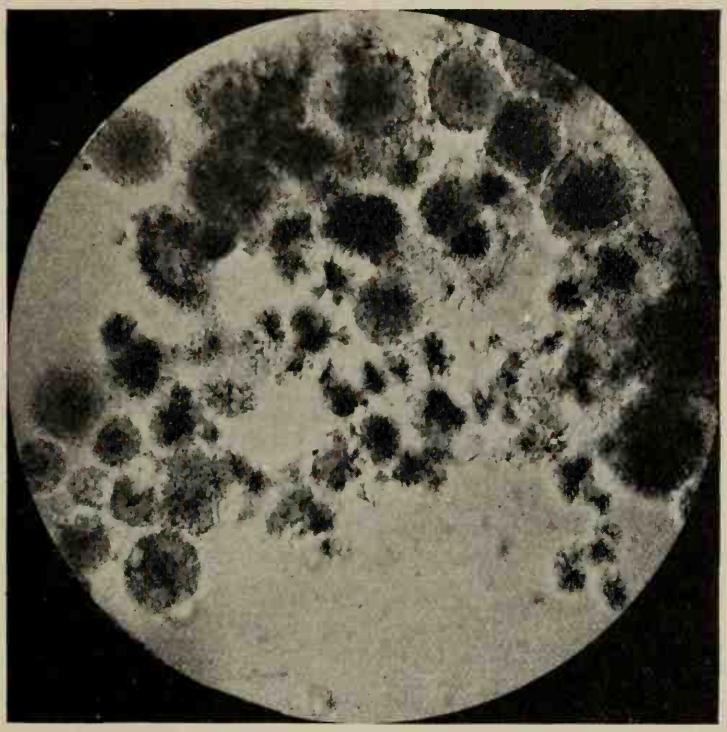

Fig. 19.—Butter containing 5 per cent of Cocoa Nut Oil. 200 diam.

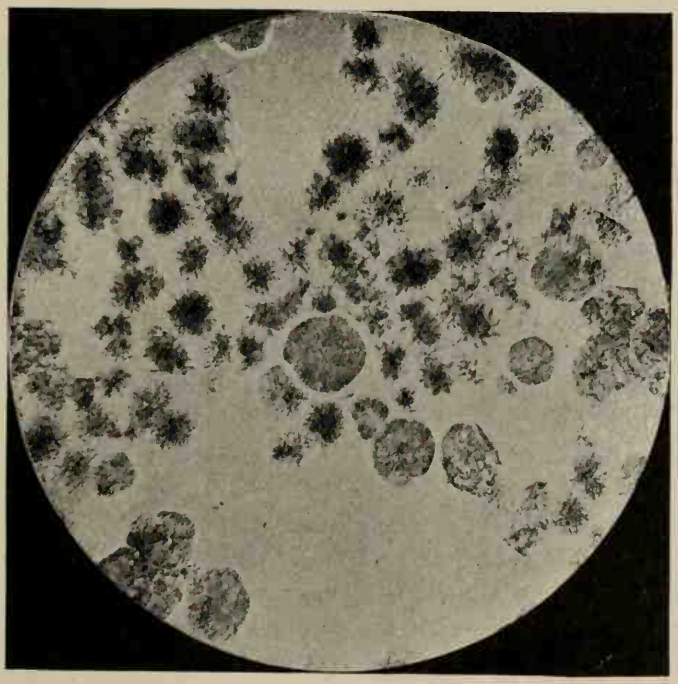

Fig. 20.—Butter containing 10 per cent of Cocoa Nut Oil. 200 diam.

they do not furnish better results than can be obtained by the methods detailed above.

There may, however, be mentioned specifically two methods published recently by *Fendler*[1] as they embody new principles, although it is hardly likely that they will supersede the foregoing methods (viz. *Müntz* and *Coudon's*, and *Polenske's*). The first method is carried out in conjunction with the determination of the *Reichert-Meissl* value. *Fendler* dissolves those fatty acids from 5 grams of butter fat, which are left after distilling off the volatile acids by the *Reichert* process, in 50 c.c. of petroleum ether, distributes 25 c.c. of the petroleum ether solution over 10 grams of powdered and dried pumice, evaporates off carefully the petroleum ether, and treats with 50 c.c. of alcohol of the specific gravity 0·9123 at 15° C. (60 per cent by volume). An accurately measured portion of the alcoholic filtrate is then titrated with decinormal alkali, and thus the amount of c.c. of decinormal alkali required to saturate the non-volatile acids obtained by the described process is calculated. Pure butter fat requires under these conditions 40 to 48 c.c. of decinormal alkali, whereas palm nut oil requires 188 c.c. and cocoa nut oil from 192 to 205 c.c. The second method is based on the determination of the ethylesters boiling up to 300° C. For this second method cp. Vol. I. Chap. XII.

If vegetable fats have been proved to be absent, and yet *Reichert-Meissl* values are obtained which leave a doubt as to the genuineness of the butter, then only admixture of *animal* fats can be suspected. In that case, corroborative evidence should be sought in the determination of the saponification value.

Saponification Value

As indicated in the table (p. 669) the mean saponification value of butter fat may be taken as 227.

Butter fats that yield abnormal *Reichert-Meissl* values also give abnormal saponification values, so that, to take an example, the saponification value may drop in the last stages of lactation to 218·5. It need hardly be repeated here that a correct saponification value alone is no proof of purity, for it is very easy to prepare mixtures of oleomargarine and cocoa nut oil having the mean saponification value of 227. The saponification value is best collated with the *Reichert* value. It has been shown above (p. 693) that when an abnormally high saponification value is associated with a low *Reichert* value, the presence of cocoa nut oil may be suspected. This, however, must not be looked upon as a rule, for *Olig* and *Tillman*[2] have shown that some undoubtedly genuine Dutch butters behave abnormally, in that high *Reichert-Meissl* values are associated with low saponification values, and *vice versa*. Thus, a butter of the *Reichert-Meissl* value

[1] *Arbeiten a. d. pharm. Institut der Universität Berlin*, 1908. The author states that the method had been worked out in 1903.

[2] *Zeit. f. Unters. Nahr. Genussm.* 1906, xi. 86.

30·1 had the saponification value 224·6, and butter of the *Reichert-Meissl* value 26·1 had the saponification value 232·6. Abnormalities (if such a name be permitted) of this kind can only be due to the butter fat in the latter case containing a larger amount of myristic and lauric acid than in the former (see below).

It should not be forgotten that the saponification value depends on the vagaries of butter fat in the same manner as does the *Reichert-Meissl* value. Thus the above-mentioned abnormal butters, described under the heading of "Idiosyncrasy," gave the following values :—

Saponification Value.	Reichert-Meissl Value.	Mean Molecular Weight of the Insoluble Fatty Acids.
209·0	17·6	269·6
215·3	23·6	268·4
212·4	22·2	267·0

Butter fats having very high saponification values can be produced through feeding with turnips or turnip leaves. Thus *Siegfeld*[1] obtained in experiments made with a herd of cows, the following numbers :—

	Saponification Values.	
	Fed without Turnips.	Fed with Turnips.
Herd No. I. . .	224-235	238-241·4
Herd No. II. . .	224-230	233-242·5
Herd No. III. . .	230·6-233·1	233-243·5

Of less decisive importance for judging the purity of butter fat than the refractive index, the *Reichert-Meissl* value, the titration number of the insoluble volatile acids, and the saponification value, are the *specific gravity* and the *iodine value*. As some analysts still determine these characteristics in the examination of butter fat, either in order to obtain additional information, or in the belief that these numbers constitute valuable criteria, they must be discussed here briefly.

Specific Gravity

J. Bell, who first proposed the determination of the specific gravity as a critical test for the examination of butter fat, chose the

[1] *Zeit. f. Unters. Nahr. Genussm.* 1907, xiii. 517.

temperature of 100° F. = 37·8° C., and used an ordinary pear-shaped specific gravity bottle. In the examination of a large number of samples he found that the experimental values vary within the narrow limits of 0·911 and 0·913. In the subjoined table I collate the specific gravities of genuine butter fats and some other fats likely to be used as adulterants; all numbers refer to the temperature of 100° F.

Specific Gravities of Butter Fats and Butter Adulterants

Kind of Fat.	Specific Gravity at 100° F. = 37·8° C. (water at 37·8 = 1).	Observer.
Genuine butter fat, 113 samples .	0·911-0·913	Bell
,, ,, ,, 357 ,, .	0·9101-0·9130	Thorpe
,, ,, ,, 368 ,, .	0·9100-0·9200	v. Rijn
Mutton suet	0·90283	Bell
Beef suet	0·90372	,,
Oleomargarine	0·90136-0·90384	,,
Cocoa nut oil	0·910-0·9167	(cp. p. 522)
Lard	0·905-0·907	,, 578

From the last table, as also from the table given in Vol. I. Chap. V., the fact will be gathered that cocoa nut and palm nut oils, if present in small quantities, cannot be detected by the specific gravity test alone. It further follows that a judiciously prepared mixture of cocoa nut oil with animal oils can be incorporated with butter fat, without being detected by an abnormal specific gravity number.

The importance which some analysts ascribe to the specific gravity test in judging butter fat is entirely unjustifiable. For this test would hardly lead to the detection of smaller quantities of an adulterant than 30 per cent, an amount which is revealed with the greatest ease by some of the foregoing methods. The overestimation still accorded to the specific gravity test dates back to the time before the more modern methods had been discovered. Since these have come into vogue the specific gravity test has lost its importance, even as a corroborative test, for such gross adulterations as can be detected with the help of the specific gravity test alone are hardly practised nowadays.

The scientific explanation for the foregoing statements must be found in the fact that the slight influence which the few per cent of volatile fatty acids exercise, is completely outbalanced by slight variations in the composition of the remaining 94 per cent of insoluble fatty acids. This may be gathered from the numbers collated in the following table :—

[TABLE

Specific Gravity of Fatty Acids occurring in Butter Fat

Acid.	At ° C.	Specific Gravity.
Butyric	20/4	0·9590
Caproic	20/4	0·9274
Caprylic . . .	20/4	0·9100
Capric	40/4	0·8858
Lauric	20/4	0·883
Lauric	60/4	0·8642
Myristic . . .	60/4	0·8584
Palmitic . . .	62/4	0·8527
Stearic	69·2/4	0·8454
Oleic	11·8/4	0·8908
Oleic	78·4/4	0·8540

Since the older literature contains a number of specific gravities to which reference is still being made, and as some countries stipulate in their laws and regulations (see p. 678) certain specific gravities, it may be found useful to have them here reproduced.

Violette[1] had stated that by means of a density determination alone butters may be rapidly sorted into three classes—viz. (*a*) those undoubtedly adulterated with margarine, or with arachis, sesamé, and poppy seed oils; (*b*) those open to suspicion; (*c*) those that may be considered practically pure.

In the light of the above given explanations this statement cannot be considered as correct.

Nothing is gained by determining the specific gravity *in vacuo* as *Violette* proposes. His numbers may, however, be recorded here :—

1 c.c. of	At 100° C. weighs *in vacuo* Grms.
Genuine butter	0·86328-0·86425
Margarine	0·85766-0·85865

Skalweit, having found that the differences in the specific gravities of butter fats, and of fats likely to be used as adulterants, are greatest at 35° C., makes his determinations at this temperature. His results are given in the following table :—

Temperature.	Lard.	Margarine.	"Butterine."	Butter Fat.
°C.				
35	0·9019	0·9017	0·9019	0·9121
50	0·8923	0·8921	0·8923	0·9017
60	0·8859	0·8857	0·8858	0·8948
70	0·8795	0·8793	0·8793	0·8879
80	0·8731	0·8729	0·8728	0·8810
90	0·8668	0·8665	0·8663	0·8741
100	0·8605	0·8601	0·8598	0·8672

[1] *Compt. rend.* 117, 856.

Other chemists prefer to determine the specific gravity at 100° C. (water at 15° C. = 1); the results recorded by the different observers agree in a satisfactory manner:—

Fat.	Koenigs.	Sell.	Allen.
			At 99° C., water 15·5 = 1.
Genuine butter . . .	0·866-0·868	0·866-0·868	0·867-0·870
Beef tallow	...	0·859-0·8605	...
Lard	...	0·860-0·8605	...
Oleomargarine	...	0·859-0·860	0·8585-0·8625
Adulterated butter . . .	0·859-0·865	0·865-0·864	...

The following specific gravities at 100° C., referring to water of 100° C. as unit, have been recorded:—

Specific Gravities at 100° C., *Water at* 100° C. = 1

Fat.	J. Bell.	Muter.	Allen.
Genuine butter fat .	0·9094-0·9140	0·9105-0·9138	0·9099-0·9132
Oleomargarine . .	0·9014-0·9038	0·903-0·906	0·902-0·905

Iodine Value

The *iodine value* is of very little importance in the examination of butter fats. This is shown, in the first instance, by the great variations in the numbers recorded in the table, p. 669. The amount of unsaturated fatty acids in a butter fat is greatly influenced by the kind of oil or fat given to the cow with the food. Since the amount of unsaturated fatty acids influences the refractometric constant (pp. 541, 683), the indications furnished by the iodine value are implicitly given by the refractometer numbers of the sample.

It should further be emphasised that all those influences which tend to reduce the amount of volatile fatty acids, apart from the influence of food, *pro tanto* increase the iodine value. Thus *Farnsteiner* and *Karsch* found the iodine value of butter fat obtained from cows that had been in milk for a long time as high as 49·7. Exceptionally high values—52·4 and 53·3—were observed recently by *Siegfeld*.[1]

Exceedingly low iodine values are obtained in the case of butter fats from cows fed on turnips and turnip leaves. *Siegfeld*[2] as also

[1] *Chem. Zeit.* 1908, 506.

[2] *Zeit. f. Unters. d. Nahr. u. Genussm.* 1907, xiii. 521.

Amberger[1] observed as low iodine values as 22·5, 23·0, 23·4, 23·8, 23·9, 26·2, 26·5, 26·7 (see above).

Of still minor importance is the determination of the *insoluble fatty acids* (+ *unsaponifiable*), and of the *mean molecular weight* of the insoluble fatty acids.

The determination of the amount of *insoluble fatty acids* (see table, p. 671) is very rarely carried out at present in the examination of butter fat, since the test has been entirely superseded by the determination of the soluble volatile acids by *Reichert's* process. Moreover, the indications furnished by this test are too uncertain to admit of fixing, even approximately, the amount of any adulterant added. Even if normal numbers are found, they afford no proof of the purity of the sample. It should further be noted that the washing out of a larger or smaller amount of lauric acid from the insoluble fatty acids causes an appreciable error and corresponding uncertainty.

The determination of the mean molecular weight of the *insoluble fatty acids* has been proposed by several observers as a critical test, but inasmuch as the *Reichert* value and the saponification values furnish implicitly the same information, no further insight into the composition of the sample is gained. Some observers have even carried out complicated calculations, without noticing that they were introducing at the outset into their equations the result they hoped to obtain.

A synopsis of a number of determinations carried out with 357 samples of English butter fats (*Thorpe*[2]) is reproduced in the following table :—

I.	II.	III.	IV.	V.	VI.	VII.
No. of Samples.	Butyro-refracto-meter at 45° C. "Degrees."	Reichert-Wollny Value.	Specific Gravity at 37·8° / 37·8° C.	Saponifica-tion Value.[3]	Insoluble Acids. Per cent.	Mean Molecular Weight of Insoluble Acids.
7	42·0	22·5	0·9101	219·65	90·1	266·9
17	41·5	23·5	0·9104	221·39	89·7	265·5
15	41·5	24·5	0·9108	223·24	89·4	265·0
27	41·3	25·5	0·9110	223·41	89·3	264·2
37	41·0	26·5	0·9113	225·39	88·9	261·9
51	40·6	27·5	0·9114	226·75	88·7	261·7
78	40·1	28·8	0·9118	228·32	88·4	260·9
56	40·1	29·5	0·9120	229·91	88·3	259·6
41	39·9	30·5	0·9123	231·43	87·9	260·1
18	39·7	31·3	0·9125	232·30	87·9	258·0
10	39·4	32·6	0·9130	232·58	87·7	257·8
357						

[1] *Zeit. f. Unters. d. Nahr. u. Genussm.* 1907, xiii. 614.
[2] *Journ. Chem. Soc.* 1904, 254.
[3] Calculated by me from the saponification-equivalents given by Thorpe.

The numbers of the foregoing table must not be taken as expressing any fixed correlation or rule which can be applied straightway to the examination of any given sample, for the *mean values* naturally obliterate the irregularities which become apparent if the analytical data, which are summarised in the horizontal lines, are considered individually for each single sample. Moreover, some few samples, which had been examined in the course of this investigation, have been left out as their data fell outside the range of the numbers which the remainder of the samples in the same horizontal line gave. For a complete study of this investigation the reader must be, therefore, referred to the analyses of the samples as given in the Blue Book.[1]

Enough has been said in the foregoing lines to point out clearly that the "rapid" methods, although undoubtedly indicating in a given case whether a genuine butter or a grossly adulterated butter is under examination, fail in certain cases to allow of definite conclusions being drawn as to whether adulteration has taken place or not. The fundamental error of some analysts consists in resting satisfied with the performance of the "rapid" tests, which apply chiefly to the 6 per cent to 7 per cent of volatile fatty acids, whereas the 94 per cent of insoluble fatty acids are not further investigated. A good deal of uncertainty is eliminated by performing the *phytosteryl acetate test*, as this test reveals unmistakably the presence of any vegetable oils and fats (cocoa nut oil, palm kernel oil) which may have been admixed to the butter as such, and also the presence of any *margarine containing vegetable oils*. It is, therefore, perfectly unnecessary to rely in the search for margarine on the assistance of the law-makers, who, in some countries, prescribe the compulsory addition of sesamé oil to margarine. In order to show how futile this palliative must be, it may be pointed out in the first instance that the adulterator, in defiance of the law, can easily prepare margarine to which no sesamé oil has been added. But even if, by careful supervision, a margarine maker could be prevented from omitting the sesamé oil, it is easy to circumvent the *Baudouin* test by employing colouring matters, which give a similar reaction to sesamé oil with hydrochloric acid alone. *Fendler*,[2] as also *Lewkowitsch* (before a Parliamentary Committee[3]), have shown that if it be attempted to wash out such colouring matters by treating the fat with hydrochloric acid, the treatment must be repeated so often that finally the fat no longer gives the *Baudouin* reaction, whether sesamé oil be present or not. As the addition of colouring matters is not forbidden, it is obvious that the enforced addition of sesamé oil to margarine cannot be of any lasting help to the analyst. On the other hand, genuine butters have occurred which faintly gave the *Baudouin* colour test. On the strength of this test these butters would have been judged to have been adulterated with margarine. The colour reaction in these butters is due to part of the chromo-

[1] *Report of the Departmental Committee on Butter*, 1904.
[2] *Chem. Revue*, 1905, 10. [3] *Report on the Butter Trade*, July 1906.

genetic substances of sesamé oil having passed into the milk fat of cows fed with sesamé cake. Although very many feeding experiments with sesamé cake have been carried out by a considerable number of observers, no concordant conclusions have been obtained. Whilst *Baumert* and *Falcke*, and *Thorpe*,[1] and others have shown that the chromogenetic substance of sesamé oil does not pass into the milk, there are a number of other observers (*Vieth*, *Siegfeld*, a. o.) who deny this fact, and state that they distinctly obtained the sesamé oil reaction with butter made from the milk of cows that had been fed on sesamé cake. Considering the idiosyncrasy of animals and the difficulty of conducting physiological experiments, it was impossible to decide in favour of either of the two conflicting opinions. New light has been thrown on this question by *Engel*,[2] who has ascertained by a number of experiments that four to five hours after feeding with sesamé oil the *Baudouin* reaction became noticeable, whilst after another six to ten hours it could not be obtained, and that it reappeared again after a further four to five hours, then to disappear entirely. Since the feeding of milch cows with sesamé cake is on the increase in the north of Europe — in consequence of the legally prescribed addition of sesamé oil to margarine—genuine butter fat exhibiting the *Baudouin* reaction may occur more frequently than hitherto. In this connection it should be remembered that *König* and *Schluckebier*[3] have proved that the feeding of pigs with sesamé cake produces fats which give the *Baudouin* reaction distinctly.

In all those cases where butter is suspected of having been adulterated with margarine containing *vegetable oils*, the phytosteryl acetate test alone is sufficient to solve the problem. The only difficulty arises when animal fats *alone* have been employed for adulterating. As the manufacture of such animal fats is not subject to the compulsory addition of sesamé oil, it is obvious that here the sesamé colour reaction offers no assistance whatever. The adulterator has used this loophole to the full, and has brought into commerce butter adulterants consisting of animal fats only. The analyses of some such adulterants, which are sold under fancy names ("lardine," "butter improver," etc.), has been given above (p. 677).

In case adulteration with these animal fats has taken place none of the foregoing "rapid" methods, nor, indeed, all of them together, and not even the phytosteryl acetate test will be able to prove that an adulteration has taken place. Certainty can only[4] be obtained by the further examination of the insoluble fatty acids. The author has commenced an examination of this kind, of which the outlines only can be given in the present incomplete state of the investigation. In the first instance the amount of *stearic acid* should be determined. Butter fat contains an insignificant amount of this acid, the author having obtained no more than 0·5 per cent. As oleomargarine yields about 20 per cent of stearic acid, and lard may yield up to 26 per cent,

[1] *Analyst*, 1898, p. 255; *Jahrbuch der Chemie*, 1898, 404.
[2] *Zeit. f. angew. Chem.* 1906, 286.
[3] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1908, xv. 642. [4] Cp., however, Appendix.

even small admixtures of beef fat or lard should be detectable. The author has further found that the determination of arachidic acid on the one hand and myristic acid on the other will prove of considerable assistance. In an investigation of this kind the "crude stearic acid," as obtained by the process described Vol. I. Chap. VIII., must not be looked upon, without further investigation, as being actually stearic acid. In some cases genuine butter fats gave under the conditions described Chap. VIII., precipitates which might in a superficial examination have been judged to be stearic acid, whereas further investigation has shown in each case that a mixture of arachidic acid with myristic acid or a mixture of stearic, myristic, and arachidic acids was present (cp. also Chap. VIII.).

Should these investigations which the author has in hand not lead to a satisfactory result, the method of fractionally distilling the methylesters of the fatty acids (see Vol. I. Chap. XII.), although more laborious, may lead to decisive results (cp. also Cocoa Nut Oil, p. 518).

Special colour reactions[1] for vegetable oils are hardly required in the examination of butter fat, and should only be used as corroborative tests. It should, however, be remembered that a positive *Halphen* test given by a butter fat does not prove the presence of cotton seed oil, since the chromogenetic body giving the *Halphen* reaction passes into the milk fat of cows fed on cotton seed cake.

Since the critical temperature of dissolution (Vol. I. Chap. V.) has been embodied by the Belgian Government amongst the official tests of butter fat, the following numbers may be added to those given already Vol. I. Chap. V. :—

Critical Temperatures of Dissolution (Crismer)

	With Alcohol 0·7967 Specific Gravity (containing 0·9 per cent of water), at 15·5° C., in Open Tube.						With Alcohol 0·8195 (8·85 per cent of water), at 15·5° C., in Sealed Tube.	Difference.
Butter	*a*	*b*	*c*	*d*	*e*	*f*		
1	54·8	54·8	54·8	54·6	54·3	53·8	100·5	45·7
2	54·5	54·5	54·5	54·2	...	...	100·5	46
3	57	57	57	...	...	...	103	46
4	54	54	...	...	...	...	100·5	46
5	50	50	...	...	...	...	105·5	45·5
6	56	...	...	...	...	..	102·5	46
7	56·5	52·2	...	...	...	...	102·5	46
8	52	52·4	56·5	52·4	51·2	...	98·2	45·7
Margarine and Mixtures								
1	78	78	...	...	...	...	124	46
2	72·2	72·2	...	...	...	...	118	45·8
3	72·5	...	...	...	...	...	118	45·5
4	78	...	...	...	...	...	123·8	45·8
5	69	...	...	...	...	...	115	46·0
6	63·8	..	...	...	...	...	109	45·2
Maize oil	70·5	...	...	...	...	...	...	...

[1] Cp. Ludwig and Haupt, *Zeit. f. Unters. Nahr. u. Genussm.* 1907, xiii. 605 ; Merl, *ibid.* 1908, xv. 529.

It is curious to note that in the case of a rancid butter the number of c.c. of $\frac{n}{20}$ KOH required to neutralise 2 c.c. of butter fat (dissolved in 20 c.c. of absolute alcohol), when added to the figure representing the critical temperature of the acid butter, gives approximately the critical temperature of the neutralised butter.[1]

No. of Samples.	*a* Mean Critical Temperature of Acid Butter. °C.	*b* c.c. of $\frac{n}{20}$ normal Alkali required for 2 c.c.	*c* Critical Temperature of Neutralised Butter. °C.	*d* Difference. *c* − *a*.
3 at 80-90° C.	88·5	7·5	96·4	7·9
14 at 90-96° C.	93·5	4·8	98·2	4·7
69 at 96-102° C.	99·12	1·2	101·7	2·6
17 at 102-106° C.	103·9	1·0		

A large number of tests based on the behaviour of butter fat with *solvents* are omitted here as being entirely useless.[2] Since, however, *Valenta's* test, Vol. I. Chap. V., is still to some extent in vogue as a preliminary test, it may be described in the form employed by *Allen*:[3] 3 c.c. of the melted fat are poured into a test-tube, an exactly equal measure of glacial acetic acid is added, and the contents of the tube heated until complete solution takes place on agitation. The liquid is then allowed to cool spontaneously whilst stirred with a thermometer, and the temperature observed at which the solution becomes turbid. The turbidity temperatures found for genuine butter fats were from 56°-61·5° C., whereas those for margarine were 98°-100° C.

Jean does not regard the turbidity as a criterion, but estimates the volume of acetic acid dissolved by the fat (Vol. I. Chap. V.).

I subjoin some of his results in the following table :—

Fat.	Acetic Acid dissolved. Per cent.
Pure butter	63·33
,, ,, with 10 per cent of cocoa nut oil .	66·66
,, ,, ,, 15 ,, ,, .	90
,, ,, ,, 28 ,, ,, .	96

With regard to a number of other methods, such as viscosimetric,[4] calorimetric,[5] cryoscopic,[6] and microscopical[7] examination,

[1] *Bullet. de l'Assoc. Belge des Chimistes*, 1897 (10), 453 ; *Analyst*, 1897, 158.

[2] Hoton (*Bull. Soc. Chim. de Belgique*, **18** (1904), 147 ; *Revue intern. falsific.* 1906, **19**, 115) showed that the solubility of butter in glacial acetic acid is not influenced by a larger or smaller proportion of glycerides of volatile acids.

[3] *Commercial Organic Analysis*, ii. 154.

[4] Killing, *Journ. Soc. Chem. Ind.* 1895, 198 ; Wender, *Journ. Amer. Chem. Soc.* 1895, 719.

[5] *Journ. Soc. Chem. Ind.* 1896, 560.

[6] Garelli and Carcano (Benzene), *Staz. Sperim. Agrar.* 1893, 77 ; Partheil, *Arch. der Pharm.* 239, 358 ; Peschges, *Arch. d. Pharm.* 239, 358 ; Pouret, *Bulletin Soc. Chim.* 1899, iii. 21, 738 ; Quartaroli, Acetic acid.

[7] Legros, *Revue intern. falsific.* 19, 159 (1906).

the reader must be referred to the original papers, as these methods have very little practical importance in the examination of butter fat, and are decidedly inferior to those described on the preceding pages.

STAG FAT

French—*Graisse de cerf.* German—*Hirschtalg.*
Italian—*Sego de cervo.*

For tables of characteristics see p. 723.

The specimen examined by *Amthor* and *Zink* [1] had the acid value 3·5 in the fresh state, and 5·9 after keeping for one year.

[1] *Zeit. f. analyt. Chem.* 1897, 4.

Physical and Chemical Characteristics of Stag Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index. Butyro-refractometer. "Degrees."	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 40° C.	Observer.
0·9670	Amthor and Zink	39-40 48	Amthor and Zink Beckurts[1] and Oelze	51-52 49-49·5	Amthor and Zink Beckurts and Oelze	199·9	Amthor and Zink	25·7 20·5	Amthor and Zink Beckurts and Oelze	1·66	Amthor and Zink	44·5	Beckurts and Oelze

[1] *Arch. d. Pharm.* 1895 (233), 429.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9685	Amthor and Zink	46-48	Amthor and Zink	50-52 49·5	Amthor and Zink Beckurts and Oelze	201·3	Amthor and Zink	23·6	Amthor and Zink

Lesser known animal fats, see table on opposite page.

B. WAXES

I. LIQUID WAXES

Two representatives only of this class are known, viz. sperm oil and Arctic sperm oil. As regards origin, smell, taste, and some colour reactions, they are in many respects very similar to blubber oils; so much so, that some writers classed them with the latter oils. On account of their different chemical composition I separated them from the blubber oils, and this classification has now been adopted generally.

The liquid waxes contain no glycerides;[1] they consist chiefly of compound esters of fatty acids and monovalent alcohols. They yield, therefore, on saponification, large quantities of "unsaponifiable matter." This characteristic readily serves to distinguish the liquid waxes from all other fixed oils. Whereas most fatty oils yield 95 per cent of fatty acids, the liquid waxes contain only from 60 to 65 per cent, the remaining 40 to 35 per cent being made up by monovalent aliphatic alcohols.

The liquid waxes are further readily distinguished from the fatty oils by their low specific gravities. It is notable that their viscosity is much less influenced by variations of temperature than is the case with fatty oils.

The liquid waxes absorb very little oxygen from the atmosphere, and therefore do not dry. On treatment with nitrous acid they give a solid or butter-like elaïdin.

Some of the (fatty) blubber oils contain notable quantities of waxes, forming, as it were, a gradual transition from pure glycerides (seal oil) to the true liquid waxes.

SPERM OIL

French—*Huile de cachalot; Huile de spermacéti.*
German—*Walratöl; Pottwaltran.* Italian—*Olio di spermaceti.*

For tables of characteristics see pp. 730, 731.

Sperm oil is obtained from the head cavities and from the blubber of the sperm whale, or cachelot, *Physeter macrocephalus*, L. On "trying" (cp. "Whale Oil," p. 376) the sperm whale on board ship,

[1] This assertion may require qualifying, for if the statements of *Fendler* and of *Dunlop* (see p. 727) be confirmed, some sperm oils would appear to contain from 13 to 25 per cent of glycerides.

ifica- alue.	Neutralisa- tion Value.	Inso Acids sapon
t.	Fatty Acids.	Per
4	...	.
8	...	.
4	...	.
.	203 [1]	.
4	206·5	94·8
6	...	9
2	...	.
.	...	.
5	210·1	.
7	205·7	.
2	201 [6]	9
1	193·7	9
4	...	9
5	200·8	.
.	...	.
.	...	.
4	199·15	95
9	203·8	.
7	...	9
3	203·4 [6]	9
3	203·3 [6]	9
1	201·4	.
0	200·5	9
6	201·4	.
3	206·5	.
7	...	.
.	...	.
6	...	.

leer have been given ab
cent palmitic, 38·5 per

the head and body blubbers are kept separate, since the oil from the head is worth more than that from the body.[1] The oils obtained from the head matter and from the body blubber differ considerably in appearance. The former, when first taken from the head of the whale, is clear and limpid, but after a short time thickens and hardens to a white mass. The latter (body oil) is, in its fresh state, a light straw-coloured oil. The oils are kept separate on board ship, but when received at the refineries they are generally mixed in their natural proportions, viz. one-third head oil and two-thirds body oil, and together submitted to the processes for separating the oil from the spermaceti.

Sperm whales yield from 5 to 145 barrels of crude oil; the average yield for the cows is about twenty-five to thirty, and for the bulls seventy-five to ninety. (Each barrel weighs about 230 lbs.)

In the refineries the crude sperm oil is allowed to stand in refrigerating chambers from ten to fourteen days at a temperature of 32° F. The partly solidified mass is then subjected to hydraulic pressure. The clear oil thus obtained is known as "winter sperm oil"; it will not congeal at 38° F., which is at present the usual commercial standard. Oils of 32° or 23° F. "cold-test" have also been prepared. The tendency is to produce oils of somewhat high cold-tests, since the lower the temperature at which the congealed oil is pressed the smaller is its yield. The amount of "winter sperm oil" of 38° F. "cold-test" is about 75 per cent of the crude oil. When 32° F. "cold-test" was the commercial standard, the yield of "winter sperm oil" was about 67 per cent. The "winter sperm oil" is usually bleached.

After the "winter sperm oil" has been pressed out, there remains in the press-bags a solid mass of brownish colour, which is again submitted to pressure at a higher temperature (about 50° to 60° F.), whereby the oil known as "spring sperm oil" is obtained. This congeals at 50° F. to 60° F. The quantity of "spring sperm oil" is about 9 per cent of the crude oil.

The press-cakes are stored for several days at a temperature of about 80° F., and in the course of a week are trimmed by revolving knives, and again submitted to a high pressure in hydraulic presses. Thereby a third grade of oil, "taut-pressed oil," is obtained, which solidifies at a temperature of 90° to 95° F. The quantity of oil of this grade is about 5 per cent of the crude oil, so that from the crude sperm oil a total of 89 per cent of refined oil is obtained. The residue in the press-cloths is crude spermaceti of a brown colour, which melts at a temperature of 110° to 115° F.

The following statistical data have been published by the United States Government :—

[1] About one to two cents per gallon.

Year.	Total production.	Exports.
	Barrels (230 lbs.).	Barrels (230 lbs.).
1860	73,708	32,792
1861	68,932	37,547
1862	55,641	27,976
1863	65,055	18,366
1864	64,372	45,000
1865	33,242	20,158
1866	36,663	10,630
1867	43,433	25,147
1868	47,174	18,916
1869	47,936	18,645
1870	55,183	22,773
1871	41,534	22,156
1872	45,201	24,344
1873	42,053	16,238
1874	32,203	18,675
1875	42,617	22,802
1876	39,811	23,600
1877	41,119	18,047
1878	43,508	32,769
1879	41,308	11,843
1880	37,614	12,283
1881	30,600	16,600
1882	29,844	13,006
1883	24,595	13,996
1884	22,099	5,143
1885	24,203	7,554
1886	23,312	3,118
1887	18,873	4,955
1888	16,265	1,345
1889	18,727	5,823
1890	14,480	2,000
1891	13,015	3,218
1892	12,944	1,787
1893	15,253	1,165
1894	16,333	1,720
1895	16,585	1,225
1896	15,124	215
1897	15,050	280
1898	12,520	1,952
1899	11,903	550
1900	18,525	1,100
1901	14,910	...
1902	21,970	470

The prices of oil per gallon fluctuated in the years 1868 to 1902 between 2 dollars in 1868, 1 dollar in 1885, and (the lowest value) 35 cents in 1896; in 1902 the price rose to 70 cents.

Refined sperm oil is a pale yellow thin oil, almost free from odour.

Hoffstätter's statement that sperm oil contains glycerides has been shown by *Allen* and by the author to be erroneous. Possibly *Hoffstätter*[1] examined an oil mixed with porpoise oil, since he found in his specimen valeric acid as well as glycerol.

[1] *Liebig's Annalen*, 91, 177.

More recently, however, *Fendler*[1] detected in a genuine sperm oil still containing spermaceti and having the saponification value of 150·3, 1·32 per cent of glycerol (confirmed by the acrolein test). It will be noted that the saponification number of this sperm oil is extremely high—higher than any numbers recorded by previous observers. *Dunlop*[2] also states that he found in a sperm oil from the body and in two oils from the head (by means of the acetin method) the following percentages of glycerol respectively :—1·36, 1·53, and 2·51. The saponification values of these oils were, in the same order, 122·0, 140·2, 144·4.

The sperm oil fatty acids, a few characteristics of which are given p. 730, appear to belong to the oleic series, as is shown by their iodine value, and by their property of yielding elaïdin with nitrous acid. The nature of the acids is as yet unknown. *Hoffstätter's* earlier statement that the fatty acids consist chiefly of physetoleic acid stands in need of confirmation. *Bull* isolated from two specimens of sperm oil 7·53 per cent of liquid fatty acids which had respectively the neutralisation values 183·4 and 187·9, and the iodine values 130·3 and 159·5.

Fendler found in a specimen of sperm oil, still containing spermaceti, 14·22 per cent of solid and 85·78 per cent of liquid fatty acids. The solid acids melted at 32·2° C. and had the neutralisation value 242·5. The liquid fatty acids had the neutralisation value 228·7 and the iodine value 75·6. An attempt to resolve the liquid fatty acids into different fractions, by distillation under diminished pressure, did not lead to definite results. The highest iodine value (fraction No. 4) was 92·0. The following table reproduces *Fendler's* results :—

Fraction No.	Boiling Point. °C.	Pressure (mm.).	Approximate Yield (c.c. from 100 c.c.).	Iodine Value.	Neutralisation Value.	Mean Molecular Weight.
1	165-185	25	8	48·5	274·8	204·4
2	185-200	,,	30	75·3	256·5	218·9
3	200-210	,,	10	87·7	241·7	232·3
4	210-220	,,	10	92·0	230·4	243·8
5	220-225	,,	10	90·0	223·4	251·4
6	225-235	,,	5	90·8	218·9	256·6
7	235-250	,,	5	78·3	213·7	262·8
8	250-260	50	4	91·6	205·7	273·0
9	260-265	,,	10	89·3	195·4	287·4

The fractions were liquid at the ordinary temperature ; only the three last fractions showed signs of crystallisation at the temperature of the freezing point of water.

Walker and *Warburton*[3] obtained in the author's laboratory from two specimens of sperm oil 2·5 and 3·7 per cent respectively of ether-insoluble brominated glycerides (Vol. I. Chap. VIII.). The insoluble

[1] *Chem. Zeit.* 1905, 555. [2] *Journ. Soc. Chem. Ind.* 1908, 63.
[3] *Analyst*, 1902, 237.

fatty acids gave in the bromide test 2·05 per cent of ether-insoluble brominated acids. *Procter* and *Bennett*[1] obtained as much as 6·3-6·5 per cent of ether-insoluble bromides. These high figures were not confirmed by *Dunlop*, who found, in good agreement with the results obtained by *Walker* and *Warburton*, 1·13-2·3 per cent ether-insoluble brominated acids.

Lewkowitsch[2] found the acetyl values of three samples of northern, "northern best," and southern sperm oil, 4·49, 6·43, and 5·25 respectively.

The nature of the alcohols of sperm oil is also unknown. The author[3] tried to resolve the mixed alcohols into their several constituents by fractional distillation of both the alcohols themselves and of their acetates, but hitherto these experiments have not led to any definite result, beyond proving that neither dodecatyl nor pentadecyl alcohol is present, and that the sperm oil alcohols belong for the most part, if not wholly, to the ethylene series, the higher members of which have been hitherto unknown.

This will be readily seen from the following table, giving the saponification values of the acetates of the five fractions into which the total amount of acetates were resolved, and the iodine values of the corresponding alcohols themselves. For the sake of comparison the theoretical numbers are given for alcohols, the presence of which might be expected.

Alcohols from Sperm Oil.	Saponific. Value of Acetate.	Iodine Value of Alcohol.
1st fraction . . .	190·2	46·48
2nd ,, . . .	183·8	63·30
3rd ,, . . .	180·7	69·80
4th ,, . . .	174·4	81·80
5th ,, . . .	161·4	84·90
Alcohol $C_{16}H_{32}O$ (unknown)	199	106·6
,, $C_{18}H_{36}O$ (unknown)	180	94·8
,, $C_{20}H_{40}O$ (unknown)	166	85·8

On heating[4] with soda lime the alcohols were for the most part converted into fatty acids, only 4-6 per cent of unchanged alcohol being recovered; these crude fatty acids had the acid value 181·7, and melted at 38°-40° C.

A more recent examination by the usual methods (*Dunlop*) led to the following numbers :—

[1] *Journ. Soc. Chem. Ind.* 1906, 798.
[2] *Analyst*, 1899, 321.
[3] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 134.
[4] *Ibid.* 1896, 41.

[TABLE

	Cold Test. ° C.	Sp. gr. at 15·5° C.	Wax Alcohols, etc. Per cent.	Iodine Value. (Wijs.)	Saponification Value.	Butyro-refractometer. "Degrees" at 25° C.	Free Acid as Oleic Acid. Per cent.	Wax Alcohols, etc.			
								Iodine Value. (Wijs.)	Melting Point. ° C.	Butyro-refractometer. "Degrees."	
										25° C.	40° C.
Sperm oil from "head matter" .	9·5	·8779	42·28	76·30	140·2	49·7	4·60	60·43	32-32·5	...	35·0
,, ,, ,, "body matter" .	8·5	·8772	42·14	92·85	124·8	54·8	1·42	83·17	24·5-25·5	47·0	39·0
,, ,, ,, "head matter" .	7	·880	41·16	70·35	144·4	50·0	1·39	53·7	31·5-32·5	...	35·0
,, ,, ,, "body matter" .	7	·8757	44·30	87·90	122·0	54·6	1·07	79·77	23-24	47·0	...
Southern sperm oil . . .	...	·8791	41·16	84·35	129·7	54·6	1·16	68·5	26·5	45·7	37·7
,, ,, ,, . . .	...	·8798	39·20	84·37	129·0	..	2·53	69·37	..	...	...

Physical and Chemical Characteristics of Sperm Oil

Specific Gravity.			Saponification Value.		Iodine value.		Reichert-Meissl Value.		Fatty Acids.		Alcohols.		Maumené Test.		Refractive Index.	
															At 20° C.	Observer.
°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.	1·4646-1·4655	Harvey[6]
															Oleo-refractometer.	
15	0·8799-0·8835	Bull	123·4-147·4	Deering, Stoddart, Allen	84	Archbutt	0·60[5]	Fendler	60-64	Allen	39-41·5	Allen	51	Archbutt	"Degrees."	Observer.
15·5	0·875-0·844	Allen	125·2[1]	Lewkowitsch	81·3	Thomson and Ballantyne					41	Lewkowitsch	45-47	Allen	−12 to −17·5	Jean
,,	0·8808	Thomson and Ballantyne	127·9	,,	86·5[3]	McIlhiney					37-41	Thomson and Ballantyne			−13	Archbutt and Deeley
20	0·8781[4]	Fendler	132·6[2]	,,	85·7-90·1	Bull					39·2[4]	Fendler	Specific. Temp. Reaction.			
99 (water at 15·5=1)	0·8303	Allen	120	Archbutt and Deeley							39·2-44·3	Dunlop			Butyro-refractometer.	
			129·2-136·9	Bull									100	Thomson and Ballantyne	°C. "Degrees."	Observer.
			132·5	Thomson and Ballantyne											25 54	White
			150·3[4]	Fendler											40 46·2	,,
			122-144·4	Dunlop												

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.	
At 15·5° C.	Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.
0·899	Allen	16·1	Archbutt and Deeley	21·4	Archbutt and Deeley	281-294	Allen	88·1	Williams
		Titer Test.		13·3	Williams	305	Williams	83·2-85·6	Lewkowitsch
		11·1-11·9	Lewkowitsch			237·7 ??	Fendler[4]		

[1] Southern sperm oil. [2] Northern sperm oil. [3] Calculated from bromine addition value 54·54 (bromine substitution value being 1·04).
[4] The specimen had the acid value 13·2 and still contained spermaceti; the solidifying and melting points of this specimen are given respectively as 15·5° C. and 18° C.
[5] *Chem. Zeit.* 1905, 555. [6] Nine samples.

Physical and Chemical Characteristics of Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
23-23·4	Lewkowitsch	25·5-27·5	Lewkowitsch	64·6-65·8	Lewkowitsch

Commercial sperm oil contains only small quantities of free fatty acids. In the following table a few numbers are recorded :—

No.	Sperm Oil.	Free Fatty Acids, as Oleic Acid. Per cent.	Observer.
1	Best quality, cold bagged .	1·46	Deering
2	Second, "hot pressed" . .	2·11	,,
3	Intermediate quality . .	0·75	,,
4	Oil of good quality . .	2·11	,,
5	Oil of doubtful quality . .	0·55	,,
6	,, ,, ,, . .	1·21	,,
7	Oil of bad quality . . .	2·06	,,
8	,, ,, . . .	2·64	Thomson and Ballantyne

Sperm oil is a valuable lubricating oil for spindles and light machinery, on account of its slight tendency to "gum," and because the viscosity does not decrease so rapidly with the increase of temperature as is the case with other lubricating oils (see Vol. III.). A sample of sperm oil examined in the writer's laboratory required in *Redwood's* viscosimeter 146·5 seconds at 70° F. (cp. also Vol. I. Chap. V.).

The comparatively high price of sperm oil invites adulteration with fatty oils or hydrocarbon oils. The detection of these adulterants is an easy task. Admixture with Arctic sperm oil, the physical and chemical characteristics of which are almost identical with those of sperm oil, is, however, very difficult to detect.

The *specific gravity* of sperm oil being very low, a high density of a sample would point to the presence of fatty oils. Mineral oils of the same specific gravity cannot, of course, be detected by the determination of this characteristic. However, a mixture of fatty oils with hydrocarbon oils, to meet the specific gravity, would require oils of so low a specific gravity that the flash point of the resulting oil would be very low indeed. The flash point of sperm oil lies in the neighbourhood of 450° F.

The *low saponification value* of most specimens of sperm oil obtained until recently, furnished a ready means of detecting added fatty oils, such as rape oil, blubber oils, etc. As, however, a judiciously added quantity of mineral oil may compensate the increase

of the saponification value due to this cause, an oil of apparently normal saponification value may result. In fact, *Lobry de Bruyn*[1] has shown that oils occur in commerce consisting of a mixture of sperm, blubber, and mineral oils. It should, however, be noted that *Fendler*, as also *Dunlop*, found the exceptionally high saponification values 150·3, 140·2, and 144·4. The saponification value alone cannot, therefore, be considered as finally proving the purity of the sample.

The presence of notable amounts of hydrocarbons can be proved with certainty, by examining the unsaponifiable matter by means of acetic anhydride,[2] as detailed Vol. I. Chap. IX. The estimation of the amount of glycerol and calculation therefrom to fatty oil would seem to be no longer admissible, since *Fendler* and *Dunlop* found notable amounts of glycerol in sperm oils looked upon by them as genuine (cp. footnote, p. 724).

Colour reactions are hardly required in the examination of sperm oil. Any of the liver oils, which may be used as an adulterant, would be detected by the sulphuric acid test, in which liver oils give a violet colouration, changing to red, whereas sperm oil yields a brown colour, changing to dark brown. The readiest way to detect liver oils is to determine the iodine value of the sample and the yield of ether-insoluble brominated fatty acids.

ARCTIC SPERM OIL—BOTTLENOSE OIL

French—*Huile de rorqual rostré.* German—*Döglingöl, Entenwalöl.*
Italian—*Olio di spermaceti artico.*

For tables of characteristics see pp. 733, 734.

Arctic sperm oil is chiefly obtained from the bottlenose whale, *Hyperöodon rostratus* and *H. diodon* (*bidens*). The principal places where these species are caught are along the edges of the ice-fields of Northern Europe, between Bear Island and Iceland. Like the sperm whale the bottlenose whale contains, in the cavity of the head, a certain amount of oil which yields spermaceti. The quantity of crude oil obtainable from the bottlenose whale varies from 4 to 12 barrels, averaging about 8 barrels. The blubber oil is, as a rule, darker in colour than sperm oil; but the deodorised Arctic sperm oil of commerce so closely simulates sperm oil, that it is practically impossible to distinguish the two oils by mere chemical examination. In the elaïdin test Arctic sperm oil yields a much softer elaïdin than sperm oil.

In commerce, however, these two oils are readily distinguished by their taste. On account of its more pronounced tendency to "gum," Arctic sperm oil is lower in price than sperm oil.

[1] *Journ. Soc. Chem. Ind.* 1894, 426.

[2] Absolute alcohol must not be used for the detection of mineral oil in the alcohols, as an ethyl alcoholic solution of the sperm alcohols, even if spirit of 0·8345 specific gravity be used, is capable of holding considerable quantities of mineral oil in solution (cp. Nash, *Analyst*, 1904, 3).

Physical and Chemical Characteristics of Arctic Sperm Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert Value.		Insoluble Fatty Acids.		Alcohols.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At ° C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	° C.	Observer.	"Degrees."	Observer.
15	0·8764	Bull	126	Deering, Allen	77·4 [1]	Mills and Akitt	1·4	Allen	61-65	Allen	37·41	Allen	42	Archbutt	– 13	Archbutt and Deeley
15·5	0·8808	Allen		Archbutt	80·4	Archbutt					36·32	Thomson and Ballantyne	41-47	Allen		
,,	0·8797	Lewkowitsch	123-134		82·1	Thomson and Ballantyne					31·7-42·3	Lewkowitsch	Specific. Temp. Reaction.			
,,	0·8799	Thomson and Ballantyne	130·4	Thomson and Ballantyne	84·5	Lewkowitsch					34·11-34·9	,,				
98-99 (water 15·5=1)	0·8274	Allen	128·4-135·9	Lewkowitsch	67·1-79·7	Bull					39·7	Archbutt and Deeley	93	Thomson and Ballantyne		
			121·5-122·3	Bull							41·1-42·6	Bull				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Per cent.	Observer.
10·1	Archbutt and Deeley	16·1	Archbutt and Deeley	82·2-83·3	Lewkowitsch
Titer Test.		10·3-10·8	Lewkowitsch		
8·3-8·8	Lewkowitsch				

[1] Calculated from the bromine value.

Physical and Chemical Characteristics of the Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
21·7-22·0	Lewkowitsch	23·5-26·5	Lewkowitsch	64·8-65·2	Lewkowitsch

Scharling, writing in the year 1848, states that Arctic sperm oil is the dodecatylester of doeglic[1] acid. It hardly needs pointing out that this statement requires confirmation. In a more recent examination *Bull* obtained from two specimens of Arctic sperm oil 5·07 per cent and 3·65 per cent of fatty acids, which had the neutralisation values 154·6, 195 (?), and the iodine values 125·6, 121·2 respectively. The iodine values of these acids are lower than the iodine values of the corresponding acids obtained from sperm oil, whereas, considering the more pronounced gumming properties of Arctic sperm oil, the reverse would have been expected. *Lewkowitsch*[2] found the acetyl values of two Arctic sperm oils 6·35 and 4·12.

The amount of free fatty acids in two samples of Arctic sperm oil examined by *Deering*, and *Thomson* and *Ballantyne*, was 2·11 and 1·97 per cent respectively. *Bull* found in two specimens 0·9 and 3·4 per cent of free fatty acids.

With regard to the flash point of the oil see Vol. I. Chap. V.

A more recent examination, by the usual methods, of two specimens of Arctic sperm oil (*Dunlop*[3]) gave the following numbers :—

[1] Bull is of the opinion that "doeglic acid" is a mixture of oleic and gadoleic acids. *Berichte*, 1906, 3570.

[2] *Analyst*, 1899, 321.

[3] *Journ. Soc. Chem. Ind.* 1908, 63.

[TABLE

	Sp. gr. at 15·5° C.	Wax Alcohols, etc. Per cent.	Iodine Value. (Wijs.)	Saponification Value.	Glycerol. Per cent.[1]	Ether-insoluble Brominated Glycerides. Per cent.	Butyro-refractometer at 25° C. "Degrees."	Free Acid as Oleic Acid. Per cent.	Wax Alcohols, etc.			
									Iodine Value. (Wijs.)	Melting Point. °C.	Butyro-refractometer. "Degrees."	
											25° C.	40° C.
1. Arctic sperm (bottlenose) . .	·8806	38·02	88·75	129·0	2·56	3·04	55·2	0·73	80·35	23·5-24	46·7	38·7
2. Arctic sperm (bottlenose) . .	·8786	39·22	82·80	124·8	2·26	...	55·3	1·43	69·4	23	46·2	38·2

[1] Having regard to the other characteristics of the oil, these numbers appear so high that they should be accepted with reserve.

The change which Arctic sperm oil undergoes on blowing with air is detailed in the following table, due to *Procter* and *Holmes*[1] :—

Hours.	Specific Gravity.	Refractive Index.	Iodine Value.
0[2]	0·885	1·4670	80·0
3	0·887	1·4672	76·0
6	0·887	1·4672	76·0
9	0·887	1·4673	76·0
12	0·887	1·4673	74·0
15	0·888	1·4675	74·0
18	0·890	1·4676	73·0
21	0·891	1·4677	71·0
24	0·892	1·4677	71·0

II. SOLID WAXES

1. VEGETABLE WAXES

Vegetable waxes (the exudations of plant leaves) seem to be widely spread over the vegetable kingdom, though they mostly occur in small quantities. With the exception of carnaüba wax, flax wax, gondang wax, and pisang wax, the nature of these waxes [opium wax (Chap. I. "Waxes"), palm wax, getah wax, ocotilla wax, cotton seed wax, sugar cane wax,[3] etc.] has been but little studied (cp. also Étard, *La Biochémie et les chlorophylles*). (See also Appendix.)

A specimen of "chlorophyll wax" (the wax accompanying chlorophyll) examined by the author melted at 73° C., and was found to consist entirely of "unsaponifiable matter" representing a higher alcohol. On boiling with acetic anhydride it gained 6·3 per cent in weight. The saponification value of the acetate was 134·6. The recovered alcohol melted at 79-80° C. and had the iodine value 5·8.

With regard to Montan Wax (Lignite Wax), Sea-weed Wax, and Peat Wax, cp. Vol. III. "Candle Manufacture."

CARNAÜBA WAX

French—*Cire de carnauba.* German—*Carnaubawachs, Cearawachs.* Italian—*Cera di carnauba.*

For table of characteristics see p. 739.

Carnaüba wax is exuded by the leaves of *Corypha cerifera*, Virey (*Copernicia cerifera*, Mart.), a palm indigenous to tropical

[1] *Journ. Soc. Chem. Ind.* 1905, 1287. [2] Original oil.

[3] It is stated that 1 ton of sugar cane yields 1 lb. of wax, which is described as melting at 82° C., solidifying at 80° C., and having the specific gravity 0·961. The chemical composition of sugar cane wax is unknown, and the statement made by earlier writers that it consists of a saturated alcohol of the formula $C_{24}H_{50}O_2$ ("cerosin") stands in need of confirmation.

South America.[1] This palm occurs in the States of Bahia, Pernambuco, Rio Grande do Norte, Piauhy, Ceara, Maranhao, and Matto Grosso. It is especially plentiful in the province of Ceara, Brazil. The wax is gathered during the months of September to March by pulling off the leaves before they have fully opened and drying them for two or three days in the sun. During these six months the leaves can be cut twice a month, a good worker cutting about 1500 leaves per day. About 2000 to 4000 leaves are required to produce 16 kilos. of wax. The white powdery mass covering the surface of the leaves is first brushed off, then scraped off, and thrown into boiling water. After fifteen to twenty minutes the wax collects on the top as a dough-like mass, and is taken off after cooling.

The crude wax, as obtained from the plant, is dirty greenish, or yellowish; it is very hard, and so brittle that it can be readily powdered.

The chief ports from which crude carnaüba wax is shipped to Europe are Ceara, Pará, Paranguá, Pernambuco, Rio de Janeiro, and St. Luiz de Maranhas. The chief places of import in Europe are Hamburg and Liverpool. The import into Hamburg in 1904 amounted to 1500 tons. Considerable quantities are also shipped to the United States. The total exports from Brazil during 1906 amounted to 2,559,247 kilos. valued at 6,316,078 (paper) milreis, as compared with the output during 1905 of 1,895,757 valued at 3,291,126 (paper) milreis. The following table gives the latest statistical data :—

	1906. Metric tons.	1907. Metric tons.
Exports from—		
Ilha do Cajueiro . . .	565	740
Fortaleza de Ceará . . .	720	802
Pernambuco	910	826
Other ports	364	411
Total exports from Brazil . .	2559	2779
Exports to—		
Germany	1563	1805
Great Britain . . .	556	585
United States of America . .	378	367
Other countries . . .	62	22

The prices of carnaüba wax are subject to great fluctuations, as the small quantities produced lend themselves readily to market speculations.

The crude carnaüba wax is refined by remelting over water and removing the dirt. In the trade the following qualities are differentiated: "chalky" carnaüba wax and "grey fatty" carnaüba wax. These terms correspond to the German trade names: "Courantgrau" and "Fettgrau." Some qualities are bleached by filtering over bleaching earth, etc. It should, however, be noted that, in order to facilitate the process of bleaching, the carnaüba wax is

[1] Cp. Brande, *Philos. Trans.* 1811, part ii.

always mixed with a certain amount of paraffin wax. This of course lowers the melting point; hence the bleached carnaüba wax of commerce is much softer than genuine carnaüba wax, and melts at about 60° C. Bleached commercial carnaüba wax rarely has a higher melting point than 74° C., which would correspond to about 5 per cent of added paraffin wax. When the percentage of paraffin wax is high the bleached commercial wax is almost white. Some makers melt ceresin with the crude carnaüba, and use bichromate and sulphuric acid as bleaching agents.

Carnaüba wax dissolves completely in ether and in boiling alcohol; on cooling, a crystalline mass, of the melting point 105° C., is deposited from the alcoholic solution. On ignition, commercial samples of carnaüba wax yielded 0·43 per cent of ash.

By subjecting carnaüba wax to repeated fractional crystallisation, *Liebermann*[1] obtained crystals of the melting point 92° C. simulating felted paper and having no lustre (differing from cochineal wax). The melting point could not be raised by further recrystallisation.

Carnaüba wax was formerly looked upon as consisting, like beeswax, chiefly of melissyl (myricyl) cerotate and small quantities of free cerotic acid and melissyl (myricyl) alcohol; the latter is easily removable by cold ethyl alcohol. *Stürcke*,[2] who carried out a very complete research into the chemistry of carnaüba wax, maintains that free cerotic acid is absent. The definite acid value, however, found by other observers undoubtedly points to its presence. According to *Stürcke*, the following are the constituents of carnaüba wax:—

(1) A hydrocarbon, melting at 59°-59·5° C. (2) An alcohol of the composition $C_{26}H_{54}O$ (ceryl alcohol), melting at 76° C. (3) Myricyl alcohol, $C_{30}H_{62}O$, melting at 90° C.[3] (4) A dihydric alcohol $C_{25}H_{52}O_2$ (cp. Vol. I. Chap. III.), melting at 103·5°-103·8° C. (5) An acid $C_{24}H_{48}O_2$ (carnaübic acid), melting at 72·5° C. (6) An hydroxy acid $C_{21}H_{42}O_3 = C_{19}H_{38}\begin{matrix}CH_2OH\\COOH\end{matrix}$, or its lactone

$$C_{19}H_{38}\begin{matrix}CH_2\\CO\end{matrix}\!\!>O.$$

Lewkowitsch[4] found the acetyl value of carnaüba wax to be 55·24.

When saponifying carnaüba wax strong alcoholic potash must be employed, and the solution must be boiled over a flame for about an hour. If more than 3-4 per cent of water are present in the alcoholic potash, soap is apt to separate which envelops unsaponified wax so that low saponification values are found. The discrepancies in the saponification numbers recorded in the table (p. 739) may thus find their explanation. If strongest alcohol is used, an amyl-alcohol solution (cp. also p. 757) of caustic potash need not be employed.

[1] *Berichte*, 1885, 1979. [2] *Liebig's Annalen*, 223, 283.
[3] Gascard (*Journ. Chem. Soc. Ind.* 1893, 955) assigns to it the formula $C_{31}H_{64}O$.
[4] *Analyst*, 1899, 321.

Physical and Chemical Characteristics of Carnaüba Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Acid Value.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Mgrms. KOH.	Observer.
15	0·999	Maskelyne	...	...	84·1	Mills and Akitt				
,,	0·990	Husemann-Hilger	...	...	85	Allen	4	Hübl	79	Hübl
90 (water 15·5 = 1)	0·8500	Allen	...	...	84	Wiesner	4-8	Allen	80-84	Allen
			80-81	Stürcke	83-83·5	Stürcke	3·4	Henriques	78·4	Henriques [4]
					85-86 [1]	,,	7·0	,,	83·4	,,
98	0·8422	,,	86-87	Schaedler	90-91 [2]	Schaedler	0·3-0·5	Berg	79·68	Lewkowitsch
					84	Radcliffe [3]	1·97	Lewkowitsch	80·38	,,
							2·9	Radcliffe	88·3	Radcliffe

Physical and Chemical Characteristics of Carnaüba Wax—continued

Iodine Value.		Alcohols+Hydrocarbons.[5]		Fatty Acids.[6]		Refractive Index. Butyro-refractometer. "Degrees."	
Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.	At 80° C. Calculated to 40° C.	Observer.
13·5	Lewkowitsch	54·87	Allen and Thomson	47·95	Lewkowitsch	65·7-69	Berg
13·2	Radcliffe	55	Stürcke				

[1] Recently purified.
[2] Old specimen.
[3] *Journ. Soc. Chem. Ind.* 1906, 158.
[4] By saponification in the cold.
[5] Specific gravity of the alcohols at 100° (water at 100° = 1) 0·8426 (Archbutt).
[6] Melting point of fatty acids 85° C. (Lewkowitsch).

Engler[1] found that a 5 per cent solution of carnaüba wax in chloroform gave a deviation of 0·1° to the right in a saccharimeter in a 200-mm. tube.

Valenta[2] examined the melting points of the following mixtures of carnaüba wax with stearic acid, ceresin, and paraffin wax :—

Proportion of Carnaüba Wax. Melting Point 85° C.	Melting Point of Mixtures of Carnaüba Wax with		
	"Stearic Acid" of Melting Point 58·5° C.	Ceresin of Melting Point 72·7° C.	Paraffin Wax of Melting Point 60·5° C.
Per cent.	°C.	°C.	°C.
5	69·75	79·10	73·90
10	73·75	80·56	79·20
15	74·55	81·60	81·10
20	75·20	82·53	81·50
25	75·80	82·95	81·70

The table shows that the addition of 5 per cent of carnaüba wax to the substances named produces a considerable increase in their melting point ; further additions, however, do not cause a proportional increase.

Stearic acid, if present in a specimen of commercial carnaüba wax, would be detected by the high acid value of the sample ; ceresin and paraffin wax, by the high percentage of unsaponifiable matter.

Carnaüba wax is employed in the manufacture of candles, polishing pastes, wax varnishes[3] (waxing coloured papers[4]), phonograph records, cable coverings, water-proofing, cerates in pharmaceutical practice, tailors' chalk, etc.

FLAX WAX[5]

French—*Cire de lin.* German—*Flachswachs.* Italian—*Cera di lino.*

The surface of the flax fibre is coated with a waxy substance which can be isolated by extraction with volatile solvents.

The flax wax so obtained is a white or yellowish-green or yellowish-brown solid substance of dull, wax-like fracture and possesses a very pronounced odour of flax. The wax dissolves with difficulty in chloroform, but is readily soluble in the usual solvents. In alcohol it is only partially soluble.

The fatty acids in flax wax consist of the saturated acids : palmitic and stearic, and of the liquid acids : oleic, linolic, and linolenic. The identity of the liquid acids was proved by the isolation of their oxidation products. The 81·3 per cent of alcohols *plus*

[1] *Chem. Zeit.* 1906, 711. [2] *Zeit. f. anal. Chemie*, 23, 257.

[3] *Journ. Soc. Chem. Ind.* 1894, 744.

[4] A. Wolberg (German patent 93,439) claims wool wax as a substitute for carnaüba wax for this purpose.

[5] Cross and Bevan, *Journ. Chem. Soc.* 1890, 196.

hydrocarbons given in the table consist in the main (to the extent of 70-80 per cent) of a solid hydrocarbon, melting at 68° C., and having the specific gravity 0·9941 at 10° C. The remainder is a mixture of phytosterol and ceryl alcohol.

Physical and Chemical Characteristics of Flax Wax[1]

Specific Gravity at 15° C.	Melting Point. ° C.	Acid Value.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. c.c. $\frac{n}{10}$ norm. KOH.	Alcohols+ Hydrocarbons. Per cent.
0·9083	61·5	54·49	101·51	9·61	9·27	81·32

GONDANG WAX[2] (GETAH WAX?)

French—*Cire de gondang* (*Cire de getah?*). German—*Gondangwachs*, (*Getahwachs*). Italian—*Cera di gondang* (*di getah*).

This wax is obtained by the Javanese from a wild fig-tree, gondang (*Ficus ceriflua*, Jungh; *Ficus subracemosa*, Bl.), by boiling the latex with water until the wax separates. The cakes of gondang wax have a chocolate colour outside, and are yellowish-white inside. The yellowish-white colour becomes gradually brown on exposure to the air. The wax is hard and shows conchoïdal fracture, but is not very friable. The crude wax is stated to form a "transition product" between india-rubber and wax. The crude wax melts at about 60° C.; it then forms an extremely viscous mass which can be drawn out in threads, and separates on standing into two layers—melted wax and a brown aqueous layer. On cooling, the wax remains viscous for some time; finally a white mass separates.

The specific gravity of the melted wax is 1·0115 at 15° C.; it softens at 55° C., but is not completely melted at 73° C. It dissolves in benzene, carbon bisulphide, chloroform, oil of turpentine, petroleum ether, as also in boiling ether, alcohol, and amyl alcohol. By purifying it with boiling alcohol, 70 per cent of the material are obtained as a white crystalline mass, melting at 61° C., soluble in boiling alcohol and insoluble in cold alcohol.

The purified wax of the melting point 61° C. consists chiefly of the ficoceryl ficocerylate.

On subjecting gondang wax to destructive distillation, an aqueous distillate containing acetic acid and propionic acid is obtained first, followed by an oily liquid containing a hydrocarbon, $C_{14}H_{26}$, a crystalline acid, melting at 54° C., of the formula $C_{12}H_{24}O_2$, and an alcohol, melting at 51° C., of the formula $C_{44}H_{88}O$.

[1] C. Hoffmeister, *Berichte*, 1903, 1047.

[2] Greshoff and Sack, *Rec. des trav. chim. des Pays-Bas*, 1901, 65.

PISANG WAX[1]

French—*Cire de Pisang.* German—*Pisangwachs, Bananenwachs.*
Italian—*Cera di Pisang.*

Pisang wax is found as a powdery mass on the leaves of *Cera Musæ*, indigenous to Java. The natives collect the wax in much the same manner as carnaüba wax is gathered, by scraping it off the leaves and melting the scrapings in boiling water. One branch, carrying about seven leaves (each on an average about 6 feet long), yields 60 grams of wax. The exported wax forms hard cakes of white, yellowish, or slightly green colour. The wax is slightly transparent, of granular crystalline fracture, and easily friable. The commercial product contains only 1 per cent of ash.

The specific gravity varies from 0·963 to 0·970; the melting point is from 78° to 81° C., and the saponification value 109.

The wax dissolves sparingly in strong boiling alcohol; it is also sparingly soluble in most solvents. It dissolves easily, however, in boiling oil of turpentine, amyl alcohol, and carbon bisulphide. At 15° C. the following quantities are retained in solution: by petroleum ether 0·1 per cent, acetone 0·5 per cent, ether 0·7 per cent, oil of turpentine 1 per cent, chloroform 1·7 per cent, and carbon bisulphide 1·8 per cent.

The wax consists of the pisangceryl ester of pisangcerylic acid. The commercial samples contain only 1 to 1·5 per cent of free fatty acids.

On subjecting the wax to destructive distillation a small quantity of aqueous distillate passes over whilst the temperature rises rapidly to 200° C. From 210° to 320° C. a buttery mass distils over, which can be separated by expression into a liquid and a solid portion. The liquid portion, after purification by sulphuric acid and re-distillation, appears to be a hydrocarbon having the formula $C_{16}H_{34}$. The solid mass after being crystallised from alcohol melts at 63·5° C., and is stated to have the composition expressed by the formula $C_{27}H_{54}O_2$.

PALM WAX

French—*Cire de palmier.* German—*Palmwachs.*
Italian—*Cera di palma.*

This wax is obtained from *Ceroxylon andicola*, Humb. (indigenous to the Andes), and *Klopstockia cerifera*, Karst. (indigenous to Columbia). These two palms exude from their trunks a wax-like mass which is collected by the natives. It is a greenish-white powder, and is purified in a somewhat crude fashion by melting over fire and boiling with

[1] Greshoff and Sack, *Rec. des trav. chim. des Pays-Bas*, 1901, 65.

water. This crude product is stated to be a mixture of pure wax with a resinous substance, which can be removed by repeated crystallisation from boiling alcohol, in which the resinous matter is readily soluble. The chemical characteristics are stated to be very similar to those of carnaüba wax. It should, however, be noted that commercial products sold as palm wax have frequently been found to be nothing else but carnaüba wax.

Madagascar Rhimba wax is furnished by the "Rhimba" tree of Madagascar. It appeared in commerce a few years ago in the shape of small irregular masses adhering to pieces of bark from the tree. Most of these masses were encrusted with woody and earthy particles; others had a smooth but dull and greyish surface resembling resins, which harden when running out from the trunks of the trees. Rhimba wax appears, therefore, to consist of a mixture of a vegetable wax and resin.

The wax from *Raphia Ruffia*, Mart., a palm indigenous to Madagascar, is obtained as a by-product in preparing the Ruffia fibres. It resembles carnaüba wax and is prepared in the same manner. Its specific gravity is 0·950 and its melting point 82° C. (*Jumelle*).[1] The wax is sparingly soluble in chloroform, ether, petroleum ether, benzene, carbon-bisulphide, and acetone. It dissolves in boiling alcohol, but separates on cooling. According to *Haller*,[2] this wax consists chiefly of an alcohol of the formula $C_{20}H_{42}O$, which is not identical with arachyl alcohol prepared from arachidic acid.

At present only small quantities have been prepared in Madagascar for the market; but should the demand increase, considerable quantities can be obtained, as the fibre yields about 10 per cent of wax.

Curcas wax occurring on the bark of *Jatropha Curcas* (see p. 186) consists, according to *Sack*,[3] of melissyl alcohol and melissyl melissate.

Lesser known vegetable waxes are the wax from *Ficus rubiginosa* (*Warren de la Rue* and *Müller*), the wax from *Antiaris toxicaria*, Lesch. (Upas-tree), ocotilla wax, and cotton seed wax.

2. ANIMAL WAXES

The animal waxes contain but small quantities of unsaturated acids and unsaturated alcohols. The acid and alcoholic constituents of beeswax, spermaceti, and insect wax belong chiefly to the saturated (aliphatic) series. Wool wax, however, has an exceptional chemical composition; some of its alcohols are derivatives of the cholesterol

[1] *Compt. rend.* 1905, cxli. 1251. [2] *Ibid.* 1907, cxliv. 594.
[3] *Chem. Centralbl.* 1906, i. 1106.

series, and its fatty acids are characterised by the facility with which they become dehydrated. Wool wax is also remarkable on account of the difficulty with which it is saponified even by alcoholic caustic potash.

Like all natural products, the individual waxes exhibit variations depending on the race of the animal, etc. This holds especially good of the different beeswaxes.

WOOL WAX[1] (WOOL GREASE)

French—*Cire de suint.* German—*Wollwachs.* Italian—*Cera di lana.*

For tables of characteristics see pp. 746, 747.

The term *wool wax* was proposed by the author for the neutral portion of raw wool fat, "wool grease," and has now been adopted by modern writers.

Wool fat, *Wool grease*, *Recovered grease*, *Brown grease*[2] (French—*Suintine*; German—*Wollfett*, *Wollschweissfett*, *Suinter*; Italian—*Grasso di lana greggio*, *sugna*) is the natural grease contained in sheep's wool. In the course of preparing the raw wool for spinning, this grease is removed by means of dilute soap (or sodium carbonate) solutions,[3] or by extraction with volatile solvents. In this country the suds from wool-scouring are usually collected in large tanks, and by acidulating with mineral acids, "brown grease," or "recovered grease,"[2] is obtained of varying composition, according as to whether the suds from the wool are kept separate or are mixed with the soap suds from the scoured woven goods, which latter process is the one adopted in those woollen mills where wool is washed, spun, and woven (cp. Vol. III. Chap. XVI. "Wool Grease").

The wool grease, obtained by extracting raw wool with volatile solvents, contains, of course, only the natural constituents, viz. free fatty acids, neutral esters, and free alcohols, in admixture with potassium salts of fatty acids.

The wool fats from various sources vary considerably within certain limits, much as other natural products do. The following table contains some characteristics of several wool fats obtained by extracting raw wool with ether:—

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 135; 1896, 14.

[2] In the United States this grease is known commercially as "Dégras."

[3] Dantzer (French patent 372,757) patents the employment of aqueous solutions containing only the water-soluble portions of wool-scouring suds.

[TABLE

Source of Wool Fat. From	Yield of Wool Fat. Per cent.	Potash Salts in Wool Fat calculated to Potassium Oleate. Per cent.	Colour.	Consistence.	Acid Value.	Saponification Value.	Alcohols (unsaponifiable). Per cent.	Observer.
1. New Zealand wool	16·6	4·9	dark red	fairly soft when fresh, becomes harder on keeping.	14·3	110·5-110·7	43·6-43·9	Herbig
2. Australian wool	16·0	4·24	brownish-yellow	fairly soft, remained so after keeping.	15·5	112·7-113·3	..	,,
3. South American wool	13·2	9·25	yellowish-olive-green	fairly hard.	13·2	98·7-98·9	43·1-43·6	,,
4. Russian wool	6·6	24·4	dirty brown	soft at 20° C.	13·9	94·2-95·9	38·7-39·1	,,
5. Australian wool			light brown	melts at 30·6° C.	27·4	100·3	55·12	Lewkowitsch

Since the valuable property of wool fat, viz. that of yielding emulsions with water which are easily absorbed by the skin, has been rediscovered,[1] the raw wool fat is purified by various (patented [2]) processes, and the refined neutral wool fat—*wool wax*—is brought into commerce either in an anhydrous state (under such names as "adeps lanæ"), or in the hydrated state (under the name "lanolin"). Other commercial names are "agnin," "alapurin," etc. (cp. Vol. III. Chap. XVI. "Wool Grease").

Anhydrous wool wax is a pale-yellow translucent substance, having a slight but not unpleasant smell (in contradistinction to raw wool grease, which is characterised by its peculiar disagreeable smell, recalling that of sheep). Its consistence is that of a thin ointment. It dissolves readily in chloroform, ether, and ethyl acetate. Although insoluble in water, it possesses the remarkable property of absorbing larger quantities of water than any other wax; even if as much as 80 parts of water be mixed with 100 parts of wax, the emulsion which is formed with water has the appearance of a perfectly homogeneous mass. A mixture of neutral wax and water, containing about 22-25 per cent of the latter, is sold in commerce under the name "lanolin" (see below).

Wool wax is not completely saponified by aqueous caustic alkalis; even prolonged boiling with alcoholic potash under ordinary pressure does not effect complete saponification. Sodium alcoholate (or absolute alcohol and metallic sodium) or alcoholic potash under pressure readily effect complete saponification (cp. Vol. I. Chap. II.).

[1] *Journ. Soc. Chem. Ind.* 1892, 136; 1896, 14.
[2] Cp. Langbeck, *Journ. Soc. Chem. Ind.* 1890, 356.

I. *Physical and Chemical Characteristics of Wool Wax* (i.e. *Esters and Free Alcohols*)

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
17	0·9449 [1]	Rosauer	30-30·2 [2]	Lewkowitsch	39-42·5	Stöckhardt	98·3	Allen	25·9-26·8 [2]	Lewkowitsch
17	0·9413 [3]	,,			36-41	Benedikt	102·4 [2]	Lewkowitsch	25·8-28·9 [2]	,,
98·5 (water 15·5=1)	0·9017	Allen			31-35 / 39-41 [2]	Lewkowitsch			17·1-17·6 [4]	,,

I. *Physical and Chemical Characteristics of Wool Wax* (i.e. *Esters and Free Alcohols*)—*continued*

Fatty Acids.		Alcohols.		Refractive Index.	
Per cent.	Observer.	Per cent.	Observer.	At 40° C.	Observer.
59·8	Lewkowitsch	43·6	Lewkowitsch	1·4781-1·4822	Utz
		51·8 [4]	,,		

[1] From anhydrous lanolin. [2] From raw wool fat. [3] From "Adeps lanæ," *Chem. Centr.* 1898, ii. 875.
[4] Prepared from "lanolin."

II. *Physical and Chemical Characteristics of the Insoluble Fatty Acids*

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value. Per cent.	Observer.
40	41·8	327·5	17	Lewkowitsch

III. *Physical and Chemical Characteristics of the Mixed Alcohols*

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.	Observer.
28 [1]	33·5 [1]	239 [1]	36 [1]	...	Lewkowitsch
	44·4-48·9 [2]	...	26·4 [2]	143·8 [2]	,,

IV. *Chemical Characteristics of the Neutral Esters*

Saponification Value.		Fatty Acids.		Alcohols.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
96·9	Lewkowitsch	56·66	Lewkowitsch	47·55	Lewkowitsch

The chemical composition of wool wax is not fully known. Wool wax evidently consists of a very complex mixture of esters and free alcohols; amongst the alcohols, cholesterol and isocholesterol occur to a large extent. Owing to the presence of high proportions of these alcohols wool wax rotates the plane of polarised light. *Walden* found the specific rotation $[\alpha]_D = +6{\cdot}7°$ at 35° C., and in a 25 per cent chloroform solution $[\alpha]_D = +8{\cdot}55°$. In a 25 per cent benzene solution *Rakusin* found $[\alpha]_D = +2{\cdot}8$.

Lewkowitsch was the first to show that the previously accepted statement, viz. that neutral wool wax is a mixture of cholesteryl (and isocholesteryl) oleates and stearates, is erroneous. The low iodine value of both the fatty acids and the alcohols precludes this altogether. The absence of palmitic and stearic acids has been confirmed later on by *Darmstädter* and *Lifschütz*.[3] Nor should *Buisine's* assertion that ceryl cerotate [4] is present be accepted without further proof, as ceryl alcohol occurs in raw wool fat in the free state. An

[1] From raw wool fat. [2] From lanolin. [3] *Berichte*, 1898, 103.

[4] G. de Sanctis, *Chem. Zeit.* 1895, 651, states that cerotic acid occurs in wool fat. According to *Darmstädter* and *Lifschütz*, the quantity of cerotic acid can only be very small.

inquiry into the nature of the components, carried out by the author,[1] has shown that the mean molecular weight of the alcohols (239), in conjunction with the low iodine value (36), points to the presence of lower saturated alcohols, since cholesterol and isocholesterol have the molec. weight 372 and the iodine absorption 68·3 (cp. Vol. I. Chap. II.). The fatty acids, owing to their low iodine absorption, cannot consist to any considerable extent of oleic acid. I have shown that they contain hydroxy acids,[2] as they easily give off the elements of water at temperatures little above 100° C., with formation of inner anhydrides or lactones, and assimilate considerable quantities of acetic anhydride, forming acetylated acids.

Marchetti[3] stated that he isolated from wool wax an alcohol of the formula $C_{12}H_{24}O$—termed lanolin alcohol. Since, however, two other alcohols described by *Darmstädter* and *Lifschütz*,[4] and supposed to form a homologous series with lanolin alcohol, have been shown to be lactones (see above), the existence of this alcohol becomes doubtful.

The results of a further examination of wool wax carried out by *Darmstädter* and *Lifschütz*[5] have been collated by me in a synoptical form in the following table[6]:—

[1] *Journ. Soc. Chem. Ind.* 1892, 136; 1896, 14. Cp. Vol. I. Chap. XI.
[2] *Ibid.* [3] *Gazz. Chimica*, 1895, 22.
[4] *Berichte*, 1895, 3133; cp. *Jahrbuch der Chemie*, vi. 375.
[5] *Berichte*, 1896, 618; 2890; *Journ. Soc. Chem. Ind.* 1896, 548; 1897, 150.
[6] *Jahrbuch der Chemie*, viii. 405.

[TABLE

Wool Wax[1] *separated by Amyl Alcohol into two Parts: A. and B*

A. Hard Portion,[1] forming about 10 to 15 per cent of the Wool Wax. Resolved into		B. Soft Portion, forming about 85 to 90 per cent of the Wool Wax. Resolved into			
			(β) Alcohols ; about 55 to 60 per cent resolved by means of Methyl Alcohol into two Fractions.		
(α) Acids, about 60 per cent.	(β) Alcohols, containing	(α) Acids, about 40 to 50 per cent, containing	1st Fraction resolved into Two Groups.		2nd Fraction, containing
			1st Group.	2nd Group.	
(1) Lanoceric acid (2) Lanopalmic acid (3) Myristic acid (4) Carnaübic acid (5) A liquid acid (6) A volatile acid	(1) Ceryl alcohol (2) Carnaübyl alcohol[2] (3) Cholesterol *Isocholesterol* is absent	(1) A liquid acid (about 40 per cent) (2) Myristic acid (3) Carnaübic acid Neither lanoceric nor lanopalmic acids were present	Containing ceryl alcohol, carnaübyl alcohol	Containing small amounts of ceryl and carnaübyl alcohols, and chiefly isocholesterol (11 per cent), differing from *Schulze's* isocholesterol as regards crystalline form, solubility, and composition, but identical with it as regards melting point and chemical reactions	Alcohol 2 *a* (3-4 per cent of B) Alcohol 2 *b* (6-7 per cent of B) Alcohol 2 *c*[3] (50-54 per cent of B)

[1] *Darmstädter* and *Lifschütz* term the hard fat A "Wool wax," but for chemical reasons the name wool wax should embrace all the neutral portions contained in wool fat.

[2] The existence of this alcohol must be doubted since Mathes and Sander (*Arch. der Pharm.* 1907 (246), 169) have shown in the preparation of melissyl alcohol from the unsaponifiable matter of laurel oil that a substance was obtained which simulated completely the carnaübyl alcohol described by *Darmstädter* and *Lifschütz*, but was found on further examination to be a mixture of a hydrocarbon, melting at 69° C., and of pure melissyl alcohol.

[3] This portion appears to contain the bulk of the water-emulsifying substances in wool fat (Lifschütz, German patent 171,178 ; cp. also Vol. III. Chap. XVI.). According to Lifschütz (*Monatsh. f. prakt. Dermatolog.* 1907, 235), this fraction would appear to contain oxycholesterol $C_{26}H_{44}O_2$, oxycholesterol ester $(C_{26}H_{43}O)_2O$, and other hitherto not identified derivatives of cholesterol.

The alcohols mentioned under B (β) do not contain cholesterol. The alcohol "2 *c*" gives the colour reactions of cholesterol, but since cholesterol itself could not be isolated, *Darmstädter* and *Lifschütz* concluded that cholesterol is only formed during the reaction, and that the alcohol "2 *c*" should be looked upon as a hydrated cholesterol, from which cholesterol and isocholesterol are obtained. Further researches are required to elucidate the complicated composition of wool wax. Since cholesterol and isocholesterol differ in their optical rotation (cholesterol being lævorotatory and isocholesterol dextrorotatory in ethereal solution), the polariscopic examination of the alcohols should lead to more definite information (Vol. I. Chap. I.). This is all the more required since in a more recent publication *Schulze*[1] maintains his earlier statements on isocholesterol.

A renewed inquiry into the work of *Darmstädter* and *Lifschütz* by *Röhman* and *Siebert*[2] has, however, proved that part of the substances which had been obtained by *Darmstädter* and *Lifschütz* are only formed in the course of, and are due to the manner of, preparing the products described by them, and that another part does not consist of chemical individuals, but of a mixture of the original substances with their products of saponification. As far as can be stated at present wool wax contains *lanocerin*, which is isolated by repeatedly boiling out wool fat with an equal amount of methyl alcohol, dissolving the undissolved portion in ether, and precipitating it with alcohol. Lanocerin appears to be the inner anhydride of lanoceric acid. With regard to carnaübyl alcohol see footnote, p. 749, and Vol. I. Chap. III.

To some extent the difference in the results obtained by the several observers may be due to the difference in the composition of the wool fats from which the wool waxes were isolated.

Lewkowitsch[3] found the acetyl value of a sample of wool wax from "lanolin" 23·3, and of the wool fat alcohols 143·8.

Owing to its property of forming an emulsion with water (which will not separate into two layers even after several years' standing), and to the ease with which it is absorbed by the skin, wool wax is used as a basis for ointments[4] and cosmetics.[5] The British and the German Pharmacopœia recognise two preparations, viz. Adeps lanæ anhydrous, *i.e.* pure wool wax, and Adeps lanæ hydrosus, *i.e.* hydrous wool wax, better known under the trade term "Lanolin." For further information on the subject of wool fat cp. Vol. III. "Wool Grease."

[1] *Berichte*, 1898, 1200.
[2] *Centrbl. f. Physiolog.* 1905, xix. No. 10.
[3] *Analyst*, 1899, 321.
[4] With regard to the solubility of mercuric bichloride, mercuric nitrate, sulphur, ferrous sulphate, ferric chloride, lead, acetate, iodine, potassium, iodide, iodoform, phenol, and camphor in lanoline, cp. G. Close, *Archives internationales de pharmacodynamie et de thérapie*, 1907, 460.
[5] Cp. P. G. Unna, *Medizinische Klinik*, 1907, No. 42.

BEESWAX [1]

French—*Cire d'abeilles.* German—*Bienenwachs.* Italian—*Cera d' api.*

For table of characteristics see p. 771.

Beeswax is secreted by the common bee, *Apis mellifera*, as also by other species of *Apis* and *Trigona*, as a product of digestion; it serves to the bees as the material for building up the honeycombs.[2]

At present the honey is removed from the combs by centrifugal machines. A complete description of modern apparatus has been given by *W. F. Reid.*[3]

The older process of preparing beeswax consisted in melting the emptied honeycombs by immersion in hot water, and filtering the liquefied wax from impurities (such as dead bees, etc.). A more modern process is to prepare the wax by expression after having melted the honeycombs and removed gross impurities by straining. The press-residue is again boiled up and pressed once more. The residue from the second expression still contains some 10 to 15 per cent of wax. Such residues are collected together in special establishments, and the wax is recovered by extraction with solvents. This product, known as "extracted beeswax," differs somewhat from the beeswax obtained by expression. It presents a dark-brown soft mass, greasy to the touch and of unpleasant odour; on boiling with water it gives up a yellow colouring matter. *Hirschel* [4] examined three genuine samples of "extracted" wax. Chemically they differed from expressed wax by having a somewhat higher acid value (23·3 to 27·1) and a much higher iodine value (31·2-39·6). In *Weinwurm's* paraffin wax- or ceresin-test (see p. 772), they behaved like samples of genuine

[1] The bibliography of beeswax arranged chronologically, and of waxes used in adulterating it, will be found *Journ. Soc. Chem. Ind.* 1892, 756.

[2] The propolis (German—"Klebwachs"), *i.e.* the wax used by the bees for sealing up the cells, consists, according to Greshoff and Sack (*Rec. trav. chim. des Pays-Bas*, 1903, 139), of 84 per cent of an aromatic resin, 12 per cent of wax, and 4 per cent of alcohol-soluble impurities. A more recent analysis of propolis by Dieterich (*Zeit. f. ang. Chem.* 1907, 1688) gave the following results:—

Volatile substances	5·96 per cent.
Alcohol-insoluble substances	12·94 ,,
Resinous substances	64·61 ,,
Wax	16·05 ,,
Volatile oils	Traces.

P. Borisch, *Pharm. Zentralhalle*, 1907 (48), 929, gives the following data:—Resinous matter insoluble in hot light petroleum spirit, but soluble in 96 per cent alcohol, 43·6 per cent; "Propolis balsam," soluble in hot light petroleum spirit and 70 per cent alcohol, 8·7 per cent; Beeswax, 27·9 per cent; Ethereal oil and Water, 6·9 per cent. The "propolis resin" is described as being brownish-black, soft, and melting at about 67° C.; after exposure for several hours to a temperature of 101° C. it assumes on cooling the consistence of hard Tolu balsam. The "propolis balsam" is described as a syrupy, golden-yellow fluid, having a strongly aromatic odour.

[3] *Journ. Soc. of Arts*, 1903, 522.

[4] *Chem. Zeit.* 1904, 212.

beeswax containing about 5 per cent of admixed paraffin wax. Since "extracted" beeswax is hardly sold in commerce as such, the following notes refer only to expressed wax, *i.e.* the yellow wax of commerce.

In order to increase the production of honey it has become the practice to place artificial combs in the beehives. These combs were originally made from genuine beeswax, but with the increased demand for beeswax, artificial combs are now being prepared from a mixture of beeswax and beeswax substitutes. At first ceresin was used for this purpose, but at present paraffin wax has taken its place. When such combs, after the removal of the honey, are melted down, then naturally the resulting wax will contain paraffin wax. Such a product must, of course, be looked upon as adulterated. Latterly stearic acid is being used in place of (or admixed with) paraffin wax (see p. 764).

The expressed wax is, as a rule, of a yellow or yellowish colour. Some commercial waxes, mostly of non-European origin, have a greenish, reddish, or brown colour. The chief sources of origin of beeswax are given in the tables, pp. 761-763. The crude beeswax, like all other natural products, varies not only with the race of the bee and the kind of food it takes, but also with the care exercised in preparing the wax. Thus, the wax obtained from bees who frequent pine forests is darker than that obtained from bees who collect the pollen from clover. Light coloured wax is considered of higher value than dark coloured, inasmuch as the former is bleached more readily than the latter. This must, however, not be taken as a general rule, as some dark waxes of foreign origin can be easily bleached.

The crude wax is subjected in wax refining works to a process of purification, followed, if required, by a process of bleaching.

The purification consists in remelting the wax in pitch pine vessels over boiling water so that the impurities (dirt, etc.) may settle out. In order to accelerate the settling process, and with a view to obviating as far as possible the troublesome emulsion which forms between the aqueous and the wax layers, dilute sulphuric acid is frequently added to the water over which the wax is heated. After thorough boiling and agitating, the contents of the vessels are allowed to rest, when clear wax rises to the top and is skimmed off to be poured into moulds. Yellow wax has the pleasant odour of honey, and is almost tasteless. At low temperatures it is brittle, and of fine granular fracture. The observation that yellow wax becomes white by repeated melting in water and by exposure to sunlight has led to the customary process of "air bleaching" or "sun bleaching" yellow wax. It was found by experience that the moisture of the air, the intensity of the light, and especially the extent of the surface that is exposed to the air, play a very important part in the process of bleaching. In order to expose as large a surface as possible, the yellow wax is usually converted into ribbons, or

strips, or granules.[1] It has also been found by experience that an admixture of 3-5 per cent of tallow or of a small quantity of oil of turpentine is capable of accelerating the process of air bleaching. It would appear that the oil of turpentine acts as an oxygen carrier, inasmuch as it gives rise to the formation of hydrogen peroxide, which is used as a bleaching agent in the production of white wax (see below). (At the same time the oil of turpentine renders the beeswax less friable.)

Owing to the slowness of the air-bleaching process, other methods are employed, such as decolourising by treatment with animal char, or with fuller's earth;[2] purely chemical processes of bleaching, viz. by means of hydrogen peroxide, ozone, potassium bichromate and sulphuric acid, and by means of sodium hypochlorite, are also frequently resorted to. Whereas air-bleached wax is suitable for every purpose for which wax is used, chemically bleached waxes, especially those obtained by treatment with potassium bichromate and sulphuric acid, or sodium hypochlorite, are not suitable for best candles. It has, therefore, become a practice in many establishments to combine the process of chemical bleaching with air bleaching, by first treating the wax with chemicals and then "finishing it off" by exposure to light and air.[3]

All waxes do not bleach equally well, much as is the case with many individual oils and fats of different origin. Belladi wax is the easiest to bleach; it is followed in this respect by Turkish wax, Chilian wax, and Smyrna wax. Gambia wax is not bleached satisfactorily by air, but can be bleached by chemicals. Brazilian wax has not hitherto been bleached successfully. Italian waxes are more difficult to bleach. Whereas bleached Belladi wax is white with a bluish tint, other waxes give a yellowish tint, or are of a greenish or greyish hue. The art of the wax bleacher consists in selecting and blending the various natural products so as to obtain a substance of desired tint, as also of the desired hardness by mixing hard and soft (such as Mogador) waxes.

Best bleached white wax is of a pure white or slightly yellowish colour. It is odourless and tasteless, has a higher specific gravity than yellow wax, and is more brittle than the latter. It is transparent at the edges; its fracture is smooth and no longer granular.

Beeswax is not greasy to the touch, but if dropped on paper in the melted state it causes a permanent transparent spot.

Beeswax[4] consists chiefly of a mixture of crude *cerotic*

[1] Perhaps an apparatus like *Laval's* emulsifier may prove useful in comminuting beeswax to granules.

[2] Weingärtner, French patent 365,555, 1906; A. Müller-Jacobs, United States patent 883,661. A. Löb, *Chem. Revue*, 1908, 81.

[3] The bleaching of wax by air was practised by the ancient Greeks and Romans. *Pliny* describes bleached wax as "cera punica." A description of the process of converting beeswax into ribbons and bleaching by exposure to air and light is given by *Dioscorides*.

[4] Brodie, *Liebig's Annalen*, 67. 180; 71. 144. Schalfejeff, *Berichte*, 9. 278; 1688. Nafzger, *Liebig's Annalen*, 224. 225; Schwalb, *ibid.* 235. 106. Marie, *Journ. Soc. Chem. Ind.* 1894, 207; 1895, 599; 1896, 362.

acid[1] and *myricin* (melissyl [myricyl] palmitate). It also contains, in small quantities, free melissic acid, $C_{30}H_{60}O_2$ (or $C_{31}H_{62}O_2$), *myricyl alcohol* (*Schwalb*),[2] uncombined *ceryl alcohol*, and another alcohol of unknown composition (perhaps psyllostearyl alcohol found by *Sundwick*[3] in bumble-bees' wax). Small quantities of unsaturated fatty acids have also been isolated. Hydrocarbons also are normal constituents of beeswax. *Schwalb* isolated two hydrocarbons—*heptacosane*, $C_{27}H_{56}$, melting at 60·5° C., and *hentriacontane*, $C_{31}H_{64}$, melting at 67° C.

With regard to the proportion of hydrocarbons in beeswax the earlier statement made by *Schwalb*, who found 5-6 per cent, is erroneous; for *A. and P. Buisine* obtained from 12·7 to 13·0 per cent of hydrocarbons. These belong partly to the ethylene series. *Mangold*[4] confirmed *Buisine's* results. *Kebler* found 12·5-14·5 per cent. More recently *Hett and Ahrens* obtained from 12·8 to 17·35 per cent of hydrocarbons (cp. p. 762). The Indian beeswaxes ("Ghedda waxes") contain on an average only 8·6 per cent of hydrocarbons. The melting points and iodine values of the hydrocarbons contained in pure beeswax are collated in the following table:—

Melting Point.	Iodine Value.	Observer.
° C.		
49·5	22·05	A. and P. Buisine
51·0	22·5	Mangold
55·2	20·1	Ahrens and Hett

Engler[5] found a 5 per cent chloroform solution of yellow beeswax to rotate the plane of polarised light to the right (10·15° in a 200-mm. tube in a saccharimeter).

Beeswax is almost insoluble in cold alcohol. Boiling alcohol dissolves the bulk of the cerotic acid and a small quantity of myricin. The alcoholic solution reddens blue litmus paper faintly; a solution of phenolphthalein made just pink by a trace of alkali is, however, instantly decolourised. On cooling, the cerotic acid separates out so completely (in the form of thin needles) that the alcoholic solution does not become turbid on adding water, a slight opalescence only being noticeable

Pure beeswax is soluble in chloroform. The best solvent for beeswax is carbon tetrachloride.

Warm ether dissolves beeswax readily; on cooling, however, a portion of the dissolved wax separates out. According to *Robineaud*,[6]

[1] Containing about 30-40 per cent of homologous acids (*Marie*). The melting point of the isolated and recrystallised "cerotic" acid is given by various observers as 78°-79° C.

[2] According to Gascard (*Journ. Soc. Chem. Ind.* 1893, 955), the myricyl alcohol from beeswax is identical with that from carnaüba wax and has the formula $C_{31}H_{64}O$.

[3] *Zeit. f. phys. Chem.* **53** (1907), 563. [4] *Journ. Soc. Chem. Ind.* 1891, 861.

[5] *Chem. Zeit.* 1906, 711. [6] Robineaud, *Dingl. Polyt. Journ.* 1862, 60.

only 50 per cent of beeswax are dissolved by ether at the ordinary temperature. Experiments made by *Buchner*[1] showed that after allowing beeswax to stand with ether at the ordinary temperature, and washing the insoluble portion, a deep yellow ethereal solution was obtained, whereas a white mass remained undissolved. The ether-soluble portion represented 30 per cent, the ether-insoluble portion 70 per cent of the original wax. The following table indicates the difference in composition of the soluble and the insoluble portions :—

	Acid Value. I.	Saponification Value. II.	Difference. II-I.	Ratio Number.
Original beeswax . .	19·5	96·2	76·7	3·93
Ether-soluble portion .	40	83·8	43·8	1·905
Ether-insoluble portion	11·7	99·1	87·5	7·5

From these numbers the conclusion must be drawn that the major portion of cerotic acid, colouring matters, and hydrocarbons, together with the minor portion of the wax esters, pass into the ether. The ether-insoluble substance contains, therefore, a small quantity of cerotic acid and the main portion of the wax esters.

The free cerotic acid cannot be extracted from beeswax by treatment with sodium carbonate or caustic alkali, as the resulting soap solution forms with the beeswax esters a complete emulsion which does not separate, even after many months' standing (similarly as in the case of wool wax).

On distilling beeswax with lime, an oil passes over (beeswax oil[2]). On subjecting beeswax to destructive distillation *Greshoff* and *Sack*[3] obtained an oily distillate which separated into a solid and a liquid portion. Tho liquid portion contained a hydrocarbon of the composition $C_{15}H_{30}$. The solid portion still contained undecomposed wax, and gave, after saponification, a solid fatty acid of the melting point 63° C. The unsaponifiable matter contained a hydrocarbon having the composition C_nH_{2n} and melting at 56° C.

Beeswax is very frequently adulterated. *Water* and *mineral matters* (such as ochre, gypsum, etc.), also *flour* and *starch*, are easily detected. Fraudulent admixture with *tallow*, *Japan wax*, *stearic acid*, *paraffin wax* and *ceresin*, *colophony* (*rosin*), *spermaceti*, *carnauba wax*, *insect wax*, and *wool wax* may be detected by the methods described below.

Previous to the detailed examination by physical and chemical tests, the crude beeswax should be boiled with water (to remove honey) and filtered in a water oven. Gross adulterants, such as

[1] *Chem. Zeit.* 1907, 571.

[2] *Liebig's Annalen*, 2. (1832) 255 ; *Journ. Soc. Chem. Ind.* 1895, 1050.

[3] *Rec. trav. chim. des Pays-Bas*, 1901, 75.

mineral matters, are thus easily detected and determined quantitatively. The determination of *water* should not be omitted.

A preliminary test for the detection of adulterants consists in dissolving the sample in chloroform (*Long*[1]). Since ceresin, paraffin wax, carnaüba wax, and wool wax are not completely soluble in this menstruum, considerable quantities of the latter may thus be detected qualitatively. It should, however, be borne in mind that bleached (white) beeswax is not readily soluble in chloroform (*Dieterich*[2]).

As a preliminary test to which the filtered wax may be submitted, refractometric examination has been recommended by *Prosio*, *Marpmann*, *Werder*,[3] and later by *Berg*.[4] Owing to the high melting point of the wax, the refraction should be determined at 75°-80° C. Since the melting point of most beeswaxes lies above 65° C., the numbers recorded in the literature on this subject for a temperature of 62° C. have been omitted in this work, as being open to serious doubts. The figures given in the table have been determined at 84° C., but were reduced by calculation to 40° C. (*Berg*). (The numbers actually observed have not been published.) Considerable quantities of carnaüba wax, colophony, ceresin, paraffin wax, and stearic acid can be preliminarily detected by the refractometric method, as will be seen from the following numbers :—

	Butyro-refractometer. Scale Divisions at 84° C., calculated to 40° C.
Commercial stearic acid	29·8-33·3
Japan wax	47·6-49·7
Carnaüba wax	65·7-69
Beeswax	42·9-45·6

As a further preliminary test the *specific gravity* of the sample should be taken. The numbers recorded in the table (p. 761) will afford the necessary guidance. Of course, the specific gravity[5] test alone does not give a final answer as to purity, since artificial compounds (see below) can easily be prepared so as to exhibit the specific gravity of a genuine beeswax.

The *melting point* of the sample should also be taken, although this test, either alone or in conjunction with the specific gravity, does not afford decisive information, inasmuch as mixtures having the specific gravity as also the melting point of genuine beeswax can be readily prepared.

Most important clues for the detection of adulteration are furnished by the determination of the *acid value* and of the *saponification value*.

The determination of the *acid value* is carried out in the usual manner (described Vol. I. Chap. VI.), by warming 3 to 4 grms. of the sample with 20 c.c. of 96 per cent alcohol in a flask until the wax

[1] *Chem. Zeit.* 9. 1504.
[2] *Ibid.* 1898, 730 ; *ibid.* 1903, 808.
[3] *Ibid.* 1898, 58.
[4] *Ibid.* 1903, 752.
[5] Mastbaum (*Zeit. f. anal. Chem.* 1902, 929) recommends a special contrivance for the determination of the specific gravity.

is melted, distributing the wax by shaking, and titrating with standardised (about half-normal) alcoholic potash, phenolphthalein being the indicator. Care must be taken that the wax remains in a melted state during the operation. If the solution is diluted with a large quantity of alcohol and kept hot, the acid value may also be determined with half-normal aqueous alkali.

The determination of the *saponification value* should be carried out with a separate quantity of wax, as unless strongest alcohol has been used in the determination of the acid value, the saponification of the wax is not easily completed. It has been pointed out already that waxes are not saponified with the same facility as are oils and fats. The difficulties encountered by some analysts in saponifying beeswax have led to a number of proposed modifications, which are altogether unnecessary if the saponification be carried out with strongest alcohol, not containing more than 3 to 4 per cent of water. The wax should be saponified with alcoholic potash prepared with alcohol of at least 96% strength. Even then the saponification cannot be considered as complete after half an hour, as experiments instituted in the author's laboratory showed that after that time saponification values of only 60 were obtained, whereas if the wax was boiled with alcoholic potash over free fire for an hour complete saponification was effected.[1] It is advisable before titrating back with acid to add 30-40 per cent of alcohol. Complete saponification is still more readily reached by employing sodium alcoholate (cp. Vol. I. Chap. II.).

Henriques' process of cold saponification does not offer any advantage. The employment of caustic soda causes difficulties, the soda soaps of beeswax fatty acids being less readily soluble than the potassium salts. Indeed, *Henriques* later on modified his method by proposing to use petroleum ether of a boiling point of not less than 120° C., and to boil the solution of wax in such petroleum ether with alcoholic caustic soda, previous to allowing to stand. The necessity of operating with a boiling solution entirely disposes of the possibility of saponifying "in the cold." It may, however, be added that correct results can be obtained by first boiling and then allowing to stand.

Buchner[2] recommends to boil in an Erlenmeyer flask attached to a Soxhlet extractor, so that concentration of the alcohol may take place intermittently.

In pure beeswax the amount of free fatty acid stands in a definite proportion to the amount present in the form of combined esters. This was pointed out first by *Hehner*,[3] and independently and almost simultaneously by *Hübl*.[4] *Hehner* calculated the amount of

[1] It is unnecessary to boil 4-8 hours, as recommended by *Berg*. In order to carry out the saponification at a higher temperature Eichhorn (*Zeit. f. anal. Chem.* 1900, 39, 640) employs amyl alcohol as a solvent. Of course, the amyl alcohol must contain neither free acid nor esters.

[2] *Chem. Zeit.* 1905, 32.

[3] *Analyst*, 1883, 16.

[4] *Dingl. Polyt. Journ.* 249 (1883), 338.

alkali used for determining the free fatty acids to "cerotic"[1] acid, on the assumption that 1 c.c. of normal KOH neutralises 0·410 grms. of free acid. The alkali used for the saponification[2] of the neutral esters —*i.e.* the difference between the saponification value and the acid value—was calculated by him to "myricin,"[1] on the assumption that 1 c.c. of normal KOH saponifies 0·676 grm. of myricin.

In the following table a number of *Hehner's* analyses are collated :—

Kind of Wax.	"Cerotic Acid."[1]	"Myricin."[1]	Total.
	Per cent.	Per cent.	Per cent.
Wax from Hertfordshire . .	14·35	88·55	102·90
,, ,, . .	14·86	85·95	100·81
,, Surrey . . .	13·22	86·02	99·24
,, Lincolnshire . .	13·56	88·16	101·72
,, Buckinghamshire .	14·64	87·10	101·74
,, Hertfordshire . .	15·02	88·83	103·85
,, New Forest . .	14·92	89·87	104·79
,, Lincolnshire . .	15·49	92·08	107·57
,, Buckinghamshire .	15·71	89·02	104·73
,, America . . .	15·16	88·09	103·25
,, Madagascar . .	13·56	88·11	101·67
,, Mauritius . .	13·04	88·28	101·32
,, ,, . .	12·17	95·68	107·85
,, ,, . .	13·72	96·02	109·74
,, Jamaica . . .	13·49	85·12	98·61
,, ,, . .	14·30	85·78	100·08
,, Mogadore . .	13·44	89·00	102·44
,, Melbourne . .	13·92	89·24	103·16
,, ,, . .	13·18	87·47	100·65
,, Sydney . . .	13·06	92·79	105·85
,, ,, . . .	13·16	88·62	101·78

Hübl expressed the results of the examination of beeswax by simply stating the acid value and the saponification value in terms of mgrms. KOH (cp. Vol. I. Chap. VI.). The acid values of a number of samples of yellow wax were found by *Hübl* from 19 to 21, mostly 20 ; and the saponification values from 92 to 97, mostly 95. *Hübl*, being of the opinion that as a rule the higher and lower values occur simultaneously, assumed that the amount of free fatty acids stood in a definite—almost constant—ratio to the amount of esters. He therefore brought the amount of alkali required for neutralising the free acid—*i.e.* the acid value—into numerical relation to the amount of alkali required to saponify the neutral esters. The difference between the saponification and the acid value was termed by him "ether value." (For reasons stated Vol. I. Chap. VI., the term "ether value" or "ester value" has been abandoned in this work.) This ratio is 20 : 75 = 3·75 (75 being the difference between

[1] The inverted commas do not occur in the original paper ; they have been added here by the author in order to avoid confusion with the chemical individuals *cerotic acid* and *myricin*.

[2] Becker (*Zeit. f. analyt. Chem.* 19, 241) was the first to employ saponification in the examination of beeswax.

the saponification value, 95, and the acid value, 20). *Hübl* found in a number of beeswaxes that this "ratio number" varied between 3·6 and 3·8, and he therefore assumed that a beeswax, the "ratio number" of which deviates much from 3·7, must be looked upon as adulterated.

From *Hehner's* numbers given above the "ratio number" 3·9 can be calculated; this is in satisfactory agreement with *Hübl's* ratio number 3·75.

Hehner's mode of expressing the results in terms of "cerotic" acid and "myricin" is not adopted in this work, and should be abandoned as resting on assumptions, the correctness of which cannot be admitted at present. It may be conceded that the mean molecular weight of 410 for "cerotic" acid of beeswax (theory 396 for cerotic acid) is quite admissible, for the author actually found in several experiments the molecular weights of the isolated acids to be from 419 to 405·6. But the calculation of the alkali used for saponification of the neutral esters to myricin is not permissible since the proportions of hydrocarbons in "normal" beeswaxes have been shown to reach as high a percentage as 13 to 17 per cent. Hence the numbers calculated for "myricin" include, besides true myricin, varying amounts of hydrocarbons, so that the average number "88" given for "myricin" would represent only about 73 to 75 per cent of true myricin and 15 to 13 per cent of hydrocarbons, provided no free alcohols (see above, p. 754) were present. It need hardly be pointed out that the definite iodine value of beeswax entirely precludes the assumption that myricin alone, or even myricin and free myricin- and ceryl-alcohols alone, occur in the neutral portion of beeswax.

Hübl's numbers, on the contrary, merely express analytical data, such as are found by direct experiment. *Hübl's* "ratio number" introduces no further assumption, since it is derived from the data obtained by two titrations.

In order to emphasise the importance of the "ratio number" for the detection of adulteration, I collate in the following table the "ratio numbers" of some substances that are likely to be used in the adulteration of beeswax. It should be observed that the acid values are arbitrarily assumed mean values.

Substance.	1	2	3	4
	Acid Value.	Saponification Value.	Difference, 2-1.	Ratio of 1 : 3. "Ratio number."
Carnaüba wax . .	2	80	78	39
Japan wax . . .	20	227	207	10·8
Insect wax . . .	3	80·4	77·4	29·1
Spermaceti . . .	Traces	130	130	...
Myrtle wax . . .	3	208	205	68·3
Tallow	4	195	191	48
Stearic acid, pure . .	195	195	0	...
,, ,, commercial	200	200	0	...
Rosin, Austrian . .	130-146	146·8-167·1	16·4-21·1	0·126-0·144
,, American . .	154·1-164·6	183·6-194	29·5-30·0	0·191-0·182
Galipot	138	174·6	36·1	0·261
Paraffin wax, ceresin[1] .	0	0	0	...

The acid and saponification values, the means of which have been given already, as also the "ratio numbers," are fairly constant for genuine beeswaxes collected from all parts of the world with the exception of those from India and China (Annam). This will be gathered from the following table, in which I have collated a large number of observations, which may be taken as representative of the beeswaxes obtainable from the localities named :—

[1] Commercial paraffins or ceresins, however, may have a definite acid value.

[TABLE

Origin.	Number of Samples.	1 Specific Gravity at 15° C.	2 Melting Point. °C.	3 Butyro-refractometer "degrees" determined at 84° C. calculated to 40° C.	4 Acid Value.	5 Saponification Value.	6 Difference, 5-4.	7 "Ratio Number."	8 Iodine Value.	9 c.c. $\frac{1}{10}$ nor. KOH required for acids soluble in 80 per cent alcohol.[1]	10 Hydrocarbons. Per cent.	Observer.
Abyssinia, crude .	...	0·958	65	...	20·8	93·5	72·7	3·5	...	...	...	Dietze
,, remelted .	...	0·958	64·2	...	18·9	94·6	75·7	4·0	...	...	...	,,
,, . Max.	5	...	64·5	44·7	21·00	101·50	80·78	4·03	12·66	5·04	...	Berg
,, . Min.			63·5	44·5	19·94	96·39	76·40	3·83	10·41	4·14	...	Berg
Algeria . . .	28	...	63·5	44·6-44·8	20-20·5	98·5-99·5	78·5-79	3·8-3·9	9-10·5	4·5-4·6	...	,,
Angola . . .	...	0·960	63·5	...	19·6	92·9	73·3	3·7	...	...	...	Dietze
Argentina . Max.	4	...	64·0	44·1	19·89	97·62	78·02	3·96	9·60	3·28	...	Berg
Argentina . Min.				43·9	19·39	96·40	76·86	3·85	9·42	3·14	...	Berg
Australia . Max.	4	...	64·5	44·3	19·25	96·95	77·70	4·04	9·71	2·24	...	,,
Australia . Min.			64·0	43·9	18·76	94·64	75·08	4·00	9·23	2·02	..	,,
Belladi . . .	24	...	64·5	44·2	20·50	95·5-98·5	76·0-78·0	3·6-3·7	8·7-9·5	3·2-3·3	...	,,
Benguela . . .	...	0·961	63	...	19·3	93·1	73·8	3·8	...	...	...	Dietze
,, . Max.	4	...	64·0	45·9	20·58	97·51	77·07	3·80	11·31	4·82	...	Berg
,, . Min.			63·5	45·2	20·31	97·02	76·93	3·74	10·76	4·79	...	Berg
Bissao . . .	...	0·959	63·5	...	20·9	95·4	74·5	3·6	...	...	...	Dietze
Bissao Wadda Max.	2	...	65·5	44·8	21·14	99·89	78·89	3·77	11·32	4·48	...	Berg
Bissao Wadda Min.			65·0	44·6	20·93	99·82	78·75	3·72	10·68	4·26	...	Berg
Brazil, I. . .	...	0·962	63·5	...	19·6	89·5	69·9	3·6	...	...	...	Dietze
,, II. . . .	...	0·963	63·5	...	18·3	90·5	72·2	3·9	...	...	...	,,
,, . . .	47	...	65·5	43·5	18·9-19·2	96·0-96·5	76·5-77·5	4·0-4·1	9·0-9·5	2·5-2·6	...	Berg
Caiffa . Max.	2	...	65·5	44·6	20·28	99·26	79·10	3·92	7·98	3·36	...	,,
Caiffa . Min.			65·0	44·4	20·16	99·10	78·82	3·89	7·39	3·14	...	,,
California . Max.	5	...	65·5	44·1	19·11	95·31	76·72	3·99	10·76	3·58	...	,,
California . Min.			65·0	44·0	18·90	94·15	75·25	3·98	9·60	3·42	...	,,
Casablanca . . .	...	0·959	63·5	...	18·6	94·8	76·2	4·1	...	...	...	Dietze
,, . Max.	5	...	63·5	44·6	21·14	100·94	81·06	4·08	13·01	5·15	...	Berg
,, . Min.			63·0	44·4	19·88	99·17	79·17	3·75	9·56	4·93	...	Berg
Chili	...	0·960	65	...	19·7	91·4	71·7	3·6	...	...	...	Dietze
,, ...	21	...	64·5	43·6	19·5-20·0	94·5-96· 0	73·5-76·0	3·7-3·8	7·0	2·9-3·0	...	Berg

[1] 50 c.c. of filtrate from 5 grms. of beeswax.

Origin.	Number of Samples.	1 Specific Gravity at 15° C.	2 Melting Point. °C.	3 Butyro-refractometer "degrees" determined at 84° C. calculated to 40° C.	4 Acid Value.	5 Saponification Value.	6 Difference, 5-4.	7 "Ratio Number."	8 Iodine Value.	9 c.c. $\frac{1}{10}$ nor. KOH required for acids soluble in 80 per cent alcohol.]	10 Hydrocarbons. Per cent.	Observer.
Chili	...	0·965	...	...	18·81	90·10	71·29	3·79	...	2·00	15·1	Ahrens & Hett
Corsica . . .	1	...	66·5	44·1	19·74	97·79	78·05	3·95	10·82	5·16	...	Berg
Cuba	...	0·961	64	...	20·2	95·2	75·0	3·7	...	...	...	Dietze
Max.	3		65·0	44·6	19·04	99·89	80·85	4·24	10·98	3·14	...	Berg
,, . Min.		...	64·0	44·0	18·20	93·24	75·04	4·12	9·46	2·12	...	Berg
Domingo, pale . .	...	0·962	63·5	...	19·8	93·5	73·7	3·7	...	...	...	Dietze
,, dark . .	...	0·960	63·5	...	20·3	94·4	74·1	3·65	...	...	...	,,
,, commercial .	...	0·960	63·5	...	20·0	93·8	73·8	3·7	...	...	...	,,
Max.	5		65·0	45·1	21·63	97·79	77·42	3·91	10·82	4·59	...	Berg
,, . Min.		...	65·0	44·6	19·81	94·64	74·69	3·52	9·84	2·68	...	Berg
,, . . .	...	0·967	...	...	20·11	93·45	73·34	3·65	...	2·69	14·25	Ahr. a. Hett
East Africa, German .	...	0·965	64	...	20·0	93·3	73·3	3·9	...	...	...	Dietze
Max.	4		64·5	44·9	21·56	102·41	80·85	4·16	9·99	5·82	...	Berg
,, ,, Min.		...	63·0	44·3	19·39	100·10	76·48	3·75	8·38	4·03	...	Berg
,, ,, . .	2	0·9489-0·9645	62·2-62·5	...	17·48-18·20	84·34-89·80	66·16-72·32	3·6-4·1	6·1-7·5	...	...	Fendler
Egypt . . .	1	...	63·4	44·0	19·49	97·11	77·62	3·98	7·98	2·80	...	Berg
Germany . . .	...	0·960-0·961	63·5	...	19-22	93-97	72-77	3·7-3·8	...	...	...	Dietze
,, . . .	1427	...	63·5-64·5	44·3-44·7	19·2-20·4	92·0-97·0	72·0-77·0	3·6-3·8	7·5-8·0	2·6-3·3	...	Berg
,, Bayern .	...	0·964	...	...	18·67	90·30	71·53	3·84	...	...	15·2	Ahr. a. Hett
,, Hanover .	...	0·966	...	...	19·08	91·20	72·12	3·78	...	...	15·2	,,
,, Hessen .	...	0·964	...	...	19·15	91·89	72·74	3·80	...	4·70	17·3	,,
,, Holstein .	...	0·965	...	...	20·40	93·85	73·45	3·65	...	4·34	15·3	,,
Max.	14				20·44	92·35	71·91	3·50	...	...	...	Buchner
,, . Min.		...	...	...	18·29	91·29	73·00	3·99	...	...	..	Buchner
Max.	4		65·5	43·9	20·16	97·51	77·42	3·85	9·19	3·02	...	Berg
Haïti . Min.		...	64·5	43·9	20·09	93·45	73·29	3·02	8·46	2·13	...	Berg
Italy . . .	77	...	64·5	44·5-44·9	21-21·5	98·0-99·0	75-77·5	3·5-3·8	10·75-12·75	5·0-6·0	...	,,

Madagascar		...	0·960	64	...	21·1	98·0	76·9	3·65	...	...	...	Dietze
,,		18	...	64·5-65	44·7-45	18·5-19·5	97·0-101·0	78·0-81·0	4·0-4·3	9·0-10·0	4·0-4·5	...	Berg
,,		...	0·970	...	...	20·30	96·80	76·50	3·77	...	5·91	12·8	Ahr. a. Hett
Mazagan, I.		...	0·962	64	...	21·7	102·8	81·0	3·8	...	...	...	Dietze
,, II.		...	0·962	64	...	22·0	102·5	80·5	3·7	...	...	...	,,
Mogador		184	...	63·5	44·4-45·0	19·6-21·5	96·5-98	76·5-78·5	3·8-4·0	10·5-12·0	5·25-4·5	...	Berg
Montenegro		...	0·960	64	...	20·2	92·7	72·5	3·6	...	...	...	Dietze
Morocco		212	...	63·5	44·7-45·2	19·8-21·3	95·5-98·0	75·5-78·5	3·75-3·95	10·5-12·7	5·3-6·1	...	Berg
,,		...	0·968	...	...	20·94	98·89	77·95	3·72	...	3·80	13·2	Ahr. a. Hett
Mozambique		...	0·958	63	...	20·0	94·0	74·0	3·7	...	...	...	Dietze
,,		1	...	64·5	44·7	20·23	101·99	81·76	4·04	11·32	3·58	...	Berg
,,		...	0·967	...	...	18·80	94·90	76·10	4·05	...	3·80	14·1	Ahr. a. Hett
Palenzia		...	...	64·0	44·2	19·40	95·00	75·60	3·80	12·05	4·26	...	Berg
Palestine	Max.	3	...	65·5	44·3	21·70	103·69	81·99	3·77	9·65	3·81	...	,,
	Min.			65·0	43·9	21·56	102·69	81·13	3·74	9·27	3·36	...	
Poland and Galicia		19	...	63·5	43·2-43·7	19·2-19·5	96·0-97·5	76·5-78·0	3·9-4·0	6·5-6·9	5·2-5·6	...	,,
Portugal		...	0·966	...	...	18·37	91·84	73·47	4·00	...	4·48	15·0	Ahr. a. Hett
,,	Max.	17	...	65·5	...	20·53	95·91	77·78	4·30	14·0	3·7	...	Mastbaum
	Min.			64·0	...	16·71	88·54	70·49	3·61	6·7	1·1	...	
Sierra Leone		1	...	64·0	44·5	21·28	101·36	80·08	3·76	8·50	3·02	...	Berg
Smyrna		1	...	64·5	44·3	21·28	97·58	76·30	3·58	10·84	3·58	...	,,
Spain	Max.	5	...	66·5	44·6	19·67	98·70	79·38	4·11	10·98	3·70	...	,,
	Min.			65·5	44·3	19·32	96·04	76·65	3·94	10·76	3·25	...	
Sweden		1	...	63·5	43·9	20·09	96·81	76·72	3·82	9·35	3·02	...	,,
Tangier, I.		...	0·959	63	...	20·6	99·4	78·8	3·8	...	...	...	Dietze
,, II.		...	0·959	63	...	20·6	100·3	79·7	3·9	...	...	...	,,
Tunis		...	0·961	64	...	20·2	95·3	74·9	3·7	...	...	...	,,
,,		1	...	65·0	44·5	18·90	91·28	72·38	3·83	9·72	3·59	...	Berg
,,		33	0·965-0·972	61-64	...	16·8-20	89·7-98·0	69·7-81·2	3·43-4·50	6·7-7·12	...	...	Bertain-chand [2]
Turkey		...	0·965	...	...	19·60	92·18	72·58	3·70	...	3·36	15·0	Ahr. a. Hett
Valdivia	Max.	5	...	65·0	43·4	20·30	96·67	77·28	3·98	9·11	2·34	...	Berg
	Min.			64·5	42·9	19·59	95·11	75·81	3·87	8·37	2·12	...	
West Africa, German		1	...	65·0	44·4	20·09	96·32	76·23	3·79	10·25	4·36	...	,,
,, ,, ,,		...	0·967	...	...	19·71	92·40	72·69	3·69	...	4·90	13·6	Ahr. a. Hett
Zanzibar		...	0·959	63	...	19·9	94·9	75·0	3·8	...	...	...	Dietze

[1] 50 c.c. of filtrate from 5 grms. of beeswax.

[2] *Bulletin de la Direction de l'Agriculture et du Commerce*, Tunis, 1898.

Most of the "ratio numbers" given in the last table lie in the neighbourhood of 3·8. From these "ratio numbers" the following conclusions may be drawn: If the saponification value of a sample of beeswax be below 92, whilst the "ratio number" is that of a pure beeswax, then *paraffin wax* or *ceresin* must be present. If the ratio number exceeds 3·8, then an admixture with Japan wax, tallow, insect wax, carnaüba wax, or spermaceti may be suspected. If the acid value be much below 20, then Japan wax is absent. If, however, the "ratio number" is less than 3·8, then "stearic" acid or rosin are present. From the foregoing table it will, however, be gathered that the "ratio number" is not so constant as has been assumed by *Hübl*. This is especially shown by the analyses of some genuine European waxes which I collate in the following table:—

Origin of Beeswax.	1	2	3	4	Observer.
	Acid Value.	Saponification Value.	Difference. 2-1.	"Ratio Number."	
Hungary . .	23	90·6	67·6	2·89	Mangold
Silesia . .	17·8	92·3	74·5	4·2	Weinwurm

It must further be borne in mind that at present artificial combs containing stearic acid are being employed in bee-hives. Hence the acid value of beeswax may be found higher. Beeswaxes obtained from such artificial honeycombs gave acid values ranging from 25 to 26 (*Weinwurm*).

All the foregoing numbers refer to yellow wax. Through bleaching, the yellow wax undergoes some changes which cause great deviations from the normal acid and saponification values. This is illustrated by the numbers I have collated in the following table. They show the changes which occur in the physical and chemical characteristics of yellow wax on being bleached by various methods. (Cp. also table, p. 771).

[TABLE

	1	2	3	4	5	6	7	8	Observer.
	Melting Point.	Acid Value.	Saponification Value.	Difference, 3-2.	"Ratio Number."	Iodine Value.	1 grm. yields Hydrogen.	Hydrocarbons.	
	°C.						c.c.	Per cent.	
Pure yellow waxes	63-64	19-21	91-95	72-74	3·78-3·52	10-11	52·5-55	13-14	Buisine
Air-bleached waxes, with addition of 3-5 per cent of tallow	63·5-64	21-23	105-115	84-92	4·00-4·00	6-7	53·5-57	11-12	,,
Pure yellow wax	63·5	20·17	93·5	73·33	3·63	10·9	53	13·5	Buisine
Same wax air-bleached, with addition of 5 per cent of oil of turpentine	63·5	20·2	100·4	80·2	3·97	6·8	54·9	12·4	,,
Same wax, bleached by hydrogen peroxide	63·5	19·87	98·4	78·53	3·90	6·3	56·1	12·5	,,
Pure yellow wax	63	20·40	95·1	74·70	3·66	11·2	54·5	14·3	Buisine
Same wax, decolourised by animal char	63	19·71	93·2	73·49	3·72	11·4	53·6	13·3	,,
,, bleached with permanganate	63·7	22·63	103·3	80·67	3·56	2·6	...	...	,,
,, ,, ,,	63·5	21·96	99·2	77·24	3·51	5·8	55·5	13·3	,,
,, ,, bichromate	63·2	21·86	98·9	77·04	3·52	7·9	51	13·2	,,
,, ,, ,,	64	23·43	107·7	84·27	3·59	1·1	53·6	11·8	,,
Beeswax, white	...	22·4	98·5	76·1	3·41	...	...	...	Henriques
,, chemically bleached	...	24	95	71	2·96	...	...	...	Allen
,, air-bleached	...	19·87	94·82	74·95	3·77	...	...	...	Buchner[1]
,, chemically bleached, I.	...	22·02	98·17	76·15	3·45	...	...	...	,,
,, ,, ,, II.	...	24·0	98·56	74·56	3·10	...	...	...	,,
,, before bleaching	...	20	95·1	75·1	3·7	...	...	...	,,
,, after bleaching	...	25·1	95·1	70·0	2·8	...	...	...	,,

[1] Buchner, *Chem. Zeit.* 1905, 32. The bleaching method employed is not stated.

"Ratio numbers" differing enormously from those given above are found in Indian and Chinese (Annamite) waxes.

A number of analyses of such beeswaxes are collated in the following table:—

Origin.		Number of Samples.	1 Specific Gravity at 15° C.	2 Melting Point. °C.	3 Butyro-refracto-meter, determined at 84° C. calculated to 40° C.	4 Acid Value.	5 Saponification Value.	6 Difference, 5-4.	7 "Ratio Number."	8 Iodine Value.	9 c.c. $\frac{1}{10}$ norm. KOH required for acids soluble in 80 per cent alcohol, by Buchner's process.	Observer.
East India[1] . . .		...	...	65	...	6·10	83·30	77·20	12·1	10	1·5	Buchner
			...	66	...	6·01	82·12	76·11	12·6	10	1·5	,,
,, ,, .	Max.	418	...	63·5	44·8	8·96	106·10	99·45	14·95	9·29	3·00	Berg
	Min.		...	63·5	44·1	6·30	93·59	86·24	10·00	7·16	2·25-2·75	Berg
	Mean		...	63·0	44·3-44·7	7·0-7·5	96·0-101·5	89·0-94·0	12·5-13·5	8·5-8·7	2·02	
Tonkin and Cochin-china	Max.	281	...	63·5	45·1	8·41	97·02	89·88	12·33	9·07	3·58	
	Min.		...	63·0	44·7	7·21	93·27	85·73	11·40	6·96	2·67	,,
Annam . . .		...	0·964	61	...	7·8	94·4	...	...	6·0	...	Bellier[2]
China . .	Max.	4	...	66·5	45·5	9·52	105·07	96·88	10·02	12·17	6·16	Berg
	Min.		...	66·0	45·4	9·03	104·37	94·85	9·96	11·98	6·08	Berg
,, ...		...	...	66	...	7·55	93·70	86·15	11·4	...	...	Buchner
,, ...		...	...	62-63	...	5·33	95·61	90·28	17·9	...	...	,,
,,	Max.	...	...	...	...	8·72	120·17	111·45	12·78	...	...	,,
	Min.		...	...	...	6·28	90·20	83·82	13·9	...	...	,,

Indian from *Apis florea* .	5											
Max.		0·953	68	...	8·9	130·5	121·6	13·66	11·4	...	D. Hooper [3]
Min.		...	63	...	6·1	88·5	82·4	13·5	6·6	...	,,
Mean		...	64·2	...	7·5	103·2	95·7	12·76	8·0	...	,,
		to									
,, *Apis dorsata* .	22										
Max.		...	67	...	10·2	105·0	94·8	9·29	9·9	...	,,
Min.		...	60	...	4·4	75·6	71·2	16·1	4·8	...	,,
Mean		0·964	63·1	...	7·0	96·2	89·2	12·7	6·7	...	,,
,, *Apis indica* .	7										
Max.		...	64	...	8·8	102·5	93·7	10·64	9·2	...	,,
Min.		...	62	...	5·0	90·0	85·0	17·0	5·3	...	,,
Mean		...	63·25	...	6·8	96·2	89·4	13·1	7·4	...	,,
,, *Trigona*, Sp.	8	Dammar or *Kotabee*									
Max.	...	...	76	...	22·9	150·0	127·1	5·5	49·6	...	,,
Min.	...	...	66	...	16·1	73·7	57·6	3·57	30·2	...	,,
Mean	...	...	70·5	...	20·8	110·4	89·6	4·34	42·2	...	,,
,, *Apis dorsata* [4]	...	0·9	62	...	6·7	97·7	91·0	13·6	8·9	...	Heymann [5]

[1] To this class of waxes belongs the wax known in commerce as "Ghedda wax." The proportion of hydrocarbons is, as a rule, 8·6 per cent (Buchner, *Chem. Zeit.* 1905, No. 7).

[2] *Ann. chim. analyt. et appl.* 1906 (**11**), 366.

[3] *Agricultural Ledger*, Calcutta, 1904 (7), p. 73. Cp. also Buchner, *Chem. Zeit.* 1906, No. 43.

[4] In Weinwurm test, perfectly clear. [5] Determined in the author's laboratory.

These beeswaxes were considered as "abnormal" since no adulterants could be detected by the usual tests. It can, however, not be doubted that the waxes from *Apis florea*, *A. dorsata*, and *A. indica*, enumerated in the last table, are genuine products of the bee, even if it were conceded that the *Trigona* waxes (from the dammar bee) are no true waxes, as they are obtained from a stingless bee, and resemble in their appearance and consistence more the propolis wax (see footnote, p. 751) than true beeswax. The beeswax from *Apis dorsata*, described last in the foregoing table, is of undoubted genuineness; it was forwarded to the author by *D. Hooper* from Calcutta as wax separated from the comb of the *Apis dorsata* from Saharanpur, United Provinces. Some of those waxes (sold as Chinese) seem to be mixtures of genuine beeswax with (Chinese) insect wax. At least, in the case of a sample of Chinese beeswax submitted to me for examination, I was able to prove that adulteration with (Chinese) insect wax had taken place. The numbers obtained in the course of the usual examination are given in the following table :—

Specific Gravity at 15°.	Acid Value.	Saponification Value.	"Ratio Number."	Iodine Value.
0·9392	9·01	87·62	8·73	11·53
At 100°.				
0·8555				

Normal acid and saponification values alone do not furnish sufficient proof of the purity of a beeswax, as it is easy to prepare mixtures having a normal "ratio number" and yet containing no beeswax whatever. This will be gathered from the following table, which gives the acid and saponification values for a mixture consisting of 37·5 parts of Japan wax, 6·5 parts of stearic acid, and 56 parts of ceresin or paraffin wax :—

	1	2	3	4	5	6	7	8	9
						Conditioning			
	Acid Value.	Saponification Value.	Difference, 2-1.	"Ratio Number."	Parts in 100.	Acid Value.	Saponification Value.	Difference, 7-6.	"Ratio Number."
Japan wax . .	20	220	200	10	37·5	7·5	84·5	75	10
"Stearic" acid .	195	195	0	...	6·5	12·7	12·7	0	...
Ceresin, paraffin wax	0	0	0	...	56·0	0	0	0	...
Mixture . .						20·2	95·2	75	3·71

The ratio number of this mixture would be 3·71. It is evident that indefinite quantities of the above mixture, or of a similarly prepared one, might be added to beeswax without being detected by merely ascertaining the acid and saponification values.[1]

The determination of the iodine value is of somewhat secondary importance in the examination of beeswax; still, it will assist in the interpretation of the results obtained by other methods, and in the detection of certain impurities.[2]

In doubtful cases further examination is required, and the following tests are recommended :—

Detection and Determination of Glycerides.[3]—Although in most cases the presence of glycerides will be detected by a higher saponification value than the normal one, still small quantities may be introduced by means of a judiciously prepared mixture of glycerides, stearic acid, and paraffin wax or ceresin. The absence of glycerides can only then be pronounced upon with certainty if no glycerol is found. The safest plan is to determine the amount of glycerol quantitatively by working with at least 20 grms. of the suspected wax. The qualitative test for glycerol is too delicate, since small quantities, such as 2 to 3 per cent of a glyceride, which may have been admixed with a yellow wax before bleaching (as is usually done on a manufacturing scale), may give a positive reaction in the acroleïn test, and thus lead to erroneous conclusions. The acroleïn test must, therefore, be confirmed by quantitative tests. The amount of glycerol multiplied by 10 gives approximately the percentage of added glyceride.

Detection of Stearic Acid.—A considerable quantity of "stearic acid" is readily detected by a high acid value of the sample, provided no compensating substances like ceresin and paraffin wax have been added. It should be borne in mind that colophony also raises the acid value (for the detection of rosin, see below). If in consequence of added paraffin wax or ceresin a normal acid value has been found, and yet stearic acid be suspected, then one of the following methods must be resorted to. They are based on the principle that on treating a sample with boiling alcohol any stearic acid present will be dissolved together with cerotic acid, but will not separate out so completely as the latter does on cooling. The following process has been suggested by *Fehling*[4] and recommended by *Röttger*:[5] 1 grm. of the sample is boiled for a few minutes with 10 c.c. of 80 per cent alcohol; after cooling, the alcoholic solution is filtered and the filtrate mixed with water. In the case of a pure beeswax the liquid is

[1] As a rule such mixtures—known under the name "Composition waxes"—are coloured by the addition of colouring matter. P. Lemaire, *Bull. Soc. Pharm. de Bordeaux*, June 1904, suggests several methods for the detection of colouring matters.

[2] According to D. Hooper (*Agricultural Ledger*, 1904, No. 7), in one district of the Punjab the strained wax is intermixed with one-eighth of its weight of sesamé oil before it is made into lumps for the market.

[3] *Thénard* proposed to detect glycerides in beeswax by isolating sebacic acid from the products of dry distillation (cp. *Liebig's Annalen*, 35. (1840), 194).

[4] *Dingl. Polyt. Journ.* 147, 227. [5] *Journ. Soc. Chem. Ind.* 1890 771.

perfectly clear, or is only slightly opalescent; but in case of adulteration with stearic acid, the liquid loses its transparency, and flocks of separated stearic acid rise to the top. This reaction is plainly perceptible even if the added stearic acid be as little as 1 per cent. It should be borne in mind that rosin also, if present, will be dissolved, and give an emulsion with water.

Jean[1] endeavours to determine stearic acid quantitatively by heating 3 to 4 grms. of the sample with 60 c.c. of 96 per cent alcohol to boiling, allowing the solution to cool, and titrating with half-normal alkali, using phenolphthalein as an indicator. The alkali used is calculated to stearic acid.

In the presence of rosin the determination would include the amount of alkali required to neutralise the rosin acids.

A combination of these two tests has been more fully worked out by *Buchner*.[2] He proceeds in the following manner: 5 grms. of the sample are placed in a round-bottomed flask and 100 c.c. of 80 per cent alcohol (prepared from 850 c.c. of 96 per cent alcohol and 190 c.c. of water) are added. The total weight of the flask and contents is then ascertained. Next, the contents of the flask are heated until the mass boils gently and are kept at this temperature for 5 minutes, with frequent shaking. The flask is then immersed in cold water whilst being constantly shaken and allowed to cool down to the ordinary temperature. The flask is weighed again and brought up to the original weight by the addition of 80 per cent alcohol. The liquid is then filtered through a plaited filter, and 50 c.c. of the filtrate are titrated with $\frac{1}{10}$ normal alcoholic potash, phenolphthalein being used as an indicator. By proceeding in this manner *Buchner* obtained the following acid values:—

	c.c. $\frac{1}{10}$ norm. KOH required for acids soluble in 80 per cent alcohol. 50 c.c. of alcohol from 5 grms. of substance.
Pure beeswax, yellow	3·6-3·9
,, ,, white	3·7-4·1
Palm wax	1·7-1·8
Carnaüba wax	0·76-0·87
Japan tallow (Japan wax)	14·93-15·3
Rosin	150·3
Stearic acid[3]	65·8
Tallow "stearine"	1·1
"Artificial waxes," having the "ratio numbers" of normal beeswax—	
I. Consisting of stearic acid, tallow stearine, and ceresin	21·40
II. Consisting of stearic acid, Japan tallow, and ceresin	17·80
III. Consisting of rosin, tallow stearine, and ceresin	22·0
Pure beeswax, mixed with 25 per cent "Artificial wax" I.	8·4
,, ,, ,, 50 ,, ,, ,, II.	11·3

[1] *Journ. Soc. Chem. Ind.* 1891, 728. [2] *Chem. Zeit.* 1895, 1422.

[3] It must be pointed out that this can only refer to commercial "stearic" acid, as pure acid exhibits much smaller values.

Physical and Chemical Characteristics of Beeswax [1]

Specific Gravity.			Solidifying Point.		Melting Point.		Acid Value.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Mgrms. KOH.	Observer.
15	0·965-0·975	Hager	60·5 [2]	Allen	63 [2]	Allen	20	Hübl	95	Hübl
,,	0·962-0·966 [2]	Dieterich	62 [6]	,,	63·5 [6]	,,	18·6 [3]	Dieterich	90·4-91·4 [3]	Dieterich
,,	0·9627-0·9656 [3]	Lewkowitsch	62·5 [7]	Lewkowitsch	63·0 [7]	,,	16·8-20·6 [2]	,,	87·8-96·2 [2]	,,
,,	0·959-0·966 [4]	Camilla	60·5-62·8 [4]	Camilla	65 [3]	Barfoed	19·02-20·6 [2]	Buisine	97-107	Becker
,,	0·959 [5]	,,	61·9-63·4 [9]	Mastbaum	69-70 [3]	Lepage	19·04-20·9 [4]	Camilla	93·5-97·1 [2]	Lewkowitsch
,,	0·964-0·970	Hett and Ahrens			63-64·4 [4]	Camilla	20·9-21·2 [5]	,,	90·1-98·89 [2]	Hett and Ahrens
					62·5-63·6 [5]	,,	20·6-21·09 [2]	Lewkowitsch		
80 (water 15·5=1)	0·8356 [2]	Allen					18·37-20·94 [2]	Hett and Ahrens		
							17-21·8 [3]	Lewkowitsch	94·2-97·6 [3]	Lewkowitsch
98	0·8221 [2]	,,								
98-99	0·827 [6]	,,								
,,	0·818	,,								

Physical and Chemical Characteristics of Beeswax—continued

Iodine Value.		Reichert-Meissl Value.		Alcohols+Hydrocarbons [10] (Unsaponifiable).		Refractive Index. Butyro-refractometer.		Fatty Acids.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	"Degrees."	Observer.	Per cent.	Observer.
8·3-11	Buisine	0·34-0·41 [4]	Camilla	55·25	Schwalb	42·9-45·6 determined at 84° C. calculated to 40° C.	Berg	46·77 [11]	Lewkowitsch
7·9-8·9	Guyer [8]	0·54 [5]	,,	52·38	Allen and Thomson				
(see p. 761)	Berg			55·58 [2]	Lewkowitsch				

[1] Cp. also tables, pp. 761-763. [2] Yellow wax. [3] White wax. [4] Italian waxes not Ligurian. [5] Ligurian wax from *Apis Ligustica spinola*.
[6] Chemically bleached. [7] Air-bleached. [8] Eleven samples of pure English waxes (*Journ. Pharm.* 1897, 308).
[9] 17 Portuguese waxes. [10] Specific gravity at 100° (water at 100°=1)=0·8239 (*Archbutt*). [11] Melting point 67·2° C.

Berg,[1] who examined a very large number of waxes by *Buchner's* method (see table, p. 761), points out that the alcoholic solution made up as described above must be allowed to stand 12 hours, as otherwise the results are discordant, and generally too high. Unless a sample be allowed to stand 12 hours, the acids dissolved by the 80 per cent alcohol are found too high by 20 to 30 per cent. It should be further pointed out that the detection of stearic acid in bleached waxes, if present only to the extent of 1 to 3 per cent, is very difficult, as chemically bleached waxes may retain small amounts of acid substances.[2]

The author obtained for genuine yellow beeswax smaller numbers than did *Buchner*. Thus a Gambia beeswax required for neutralisation of the free acids, extracted as described above, 2·39 c.c. of decinormal alkali; the isolated acid had the mean molecular weight 406, whereas the same Gambia wax adulterated with varying quantities of "stearic acid" required, of course, much higher amounts of decinormal alkali, whilst the mean molecular weights of the isolated fatty acids varied from 274·8 to 298·8. In the latter case, appreciable amounts of beeswax cerotic acid had passed into the alcoholic solution.

In doubtful cases it appears advisable to use larger quantities, then to separate the stearic acid as such,[3] and to examine it further. It need hardly be pointed out that commercial stearic acid, such as would be used for adulteration, is not pure stearic acid (cp. Vol. III. Chap. XVI.).

Detection of Ceresin and Paraffin Wax.—The examination of beeswax by the saponification process can only reveal the presence of more than 10 or 8 per cent of ceresin and (or) paraffin wax, if no other adulterant be present. If the admixture falls below 5 or even below 8 per cent, the deviations from the normal acid and saponification values become so small that by these two tests alone adulteration cannot be revealed. An excellent preliminary test for the detection of added ceresin and paraffin wax down to 3 per cent has been proposed as a qualitative test by *Weinwurm*.[4] This qualitative method is based on the fact that a hot aqueous glycerin solution dissolves the unsaponifiable matter of beeswax, whereas ceresin and paraffin wax are insoluble in it. The process is carried out as follows:—Saponify 5 grms. of the sample with 25 c.c. half-normal alcoholic potash (in a 200-c.c. flask), evaporate off the alcohol completely, add 20 c.c. of concentrated glycerin, heat on the water-bath until solution is effected, and then run in 100 c.c. of boiling water. Pure beeswax gives a more or less clear, transparent, or translucent mass, through which ordinary print can be read easily. If 5 per cent of hydrocarbons are admixed, the solution is cloudy and the print is no longer legible; in the case of an admixture of 8 per cent of hydrocarbons, a precipitate is obtained.

[1] *Chem. Zeit.* 1903, 754.

[2] Thus Medicus and Wallenstein (*Zeit. f. Unters. Nahrgs. u. Genussm.* 1902, 1092) showed that the acid value of a beeswax bleached with bichromate and sulphuric acid was as high as 24·7 (cp. also table, p. 765).

[3] Cp. Berg, *Chem. Zeit.* 1908, 779.

[4] *Chem. Zeit.* 1897, 519.

I have examined this process in my laboratory, and can recommend it as a reliable preliminary test for *pure beeswax*. Turbidity of the solution does not, however, solely indicate the presence of added ceresin or paraffin wax, since carnaüba wax and insect wax also give a turbid solution. Mixtures prepared from pure beeswax and carnaüba wax, as also mixtures from pure beeswax and (Chinese) insect wax, give as strong a turbidity as does pure beeswax containing 5 per cent of added paraffin wax (*Lewkowitsch*). Beeswax from *Apis dorsata* remains clear in the *Weinwurm* test (*Lewkowitsch*). *Berg*[1] states, however, that some East Asiatic and South Asiatic beeswaxes containing considerable amounts of melissyl (myricyl) alcohol almost invariably give a turbidity in *Weinwurm's* test.

In doubtful cases it is best to prepare for guidance solutions made up with pure beeswax, and with mixtures thereof and the suspected adulterant.

Sokoloff[2] suggests the determination of the *heat of combustion* of the sample as a method of detecting small quantities of paraffin wax. Genuine beeswaxes give a heat of combustion of 10,312 calories, whereas paraffin and ceresin gave on an average 11,234 calories. Evidently this method is a very cumbersome one, and cannot therefore be recommended.

The specific gravity test will only reveal considerable quantities of added ceresin and paraffin wax, and therefore discriminative importance cannot be assigned to it. In special cases, however, the following tables may prove of some little value :—

Specific Gravity of Mixtures of Beeswax and Paraffin Wax (Wagner)[3]

Beeswax.	Paraffin Wax.	Specific Gravity.
Per cent.	Per cent.	
0	100	0·871
25	75	0·893
50	50	0·920
75	25	0·942
80	20	0·948
100	0	0·969

[1] *Chem. Zeit.* 1903, 753. [2] *Journ. Phys. Chem. Soc. Russ.* 1905 (37), 818.
[3] *Zeits. f. analyt. Chem.* 5, 280.

[TABLE

Specific Gravity of Mixtures of Beeswax and Ceresin (Dieterich)[1]

Yellow Wax.	Yellow Ceresin.	Spec. Grav. of Mixture.	White Wax.	White Ceresin.	Spec. Grav. of Mixture.
Per cent.	Per cent.		Per cent.	Per cent.	
100	0	0·963	100	0	0·973
90	10	0·961	90	10	0·968
80	20	0·9575	80	20	0·962
70	30	0·953	70	30	0·956
60	40	0·950	60	40	0·954
50	50	0·944	50	50	0·946
40	60	0·937	40	60	0·938
30	70	0·933	30	70	0·934
20	80	0·931	20	80	0·932
10	90	0·929	10	90	0·930
0	100	0·922	0	100	0·918

Considerable quantities of added ceresin and paraffin wax may be detected by the determination of the unsaponifiable matter, *i.e.* alcohols + hydrocarbons. (It has been pointed out already that the unsaponifiable portion must be determined with certain precautions, which are detailed in Vol. I. Chap. VI.) It should be borne in mind that the amount of "unsaponifiable" in different beeswaxes varies within somewhat wide limits. The numbers given in the table of characteristics fluctuate between 52·38 and 55·58. In the examination of 21 samples of beeswax, *Werder*[2] arrived at numbers lying between 48·55 and 53·08 per cent. In view of the tediousness of this process, and the uncertainty of the conclusions to be derived therefrom, it cannot be recommended for the quantitative estimation of added ceresin or paraffin wax unless it be corroborated and supplemented by other tests.

The proportion of total hydrocarbons in beeswax is accurately determined by *A. and P. Buisine's* process (Vol. I. Chap. IX.):—2 to 10 grms. of the sample are heated with potash-lime to 250° C.; the residue is powdered, and extracted in a Soxhlet extractor with dry ether or dry petroleum ether. The extract is filtered, if necessary, the solvent evaporated off, and the residue dried and weighed. The proportion of hydrocarbons in genuine yellow beeswax varies, according to *Buisine*, from 12·7 to 13 per cent, and according to *Kebler*, from 12·5 to 14·5 per cent.

Adulteration with 3 per cent of foreign hydrocarbons can thus be detected, as an easy calculation will show. The liberated hydrogen may also be measured and calculated to melissyl alcohol. 1 grm. of pure beeswax should yield from 53·5-57·5 c.c. of hydrogen, corresponding to 52·5-56·5 per cent of melissyl alcohol. In case the determination of the latter be not required, the apparatus for collecting and measuring the gas need not be employed.

[1] Wagner's *Jahresbericht*, 1882, 1028.

[2] *Chem. Zeit.* 1900, 967.

More recent determinations by *Ahrens and Hett* have, however, shown that the amount of hydrocarbons in beeswax may rise as high as 17·3 per cent (cp. table, p. 754), so that the certainty afforded hitherto by *Buisine's* test for the detection of 3 per cent of hydrocarbons becomes somewhat illusory (cp. also proportion of hydrocarbons in Ghedda waxes, p. 754).

For some alterations proposed by *Ahrens and Hett* in *Buisine's* arrangement of apparatus, the reader may be referred to the original paper, and it need only be pointed out that for the successful carrying out of *Buisine's* test the potassium hydrate should not be finely powdered, since a fine powder is apt to form lumps when the wax is poured over it. Thus unattacked wax may rise in the tube and escape decomposition.

Detection of Rosin.—The presence of rosin is detected with certainty by the *Liebermann-Storch* colour test. In the case of a dark-coloured wax it is advisable to extract the wax with alcohol, and test the residue obtained after evaporating the alcohol. If a 50 per cent alcohol be used and the alcoholic solution be filtered in the cold, any stearic acid present is not extracted. Approximately quantitative results are therefore obtainable if the residue left after evaporating off the 50 per cent alcohol be weighed. More accurate results are arrived at by determining (by *Twitchell's* method) the rosin in the alcoholic extract.

Detection of Spermaceti.—Spermaceti does not affect the acid value (cp. table, p. 760). If considerable quantities of spermaceti be present in beeswax as the only foreign wax, its presence would be detected, and its quantity can be ascertained approximately, by acetylating the isolated unsaponifiable matter. In more complicated cases the alcohols must be examined thoroughly by the methods given in Vol. I. Chap. IX. The quantity of spermaceti can then be derived from the quantity of palmitic acid obtained by the conversion of cetyl alcohol into this acid (cp. Vol. I. Chap. IX.). Such elaborate methods must be especially resorted to in the case of cerates and of wax polishes (see Vol. III. Chap. XVI. Cp. also "Beeswax Candles," Vol. III. Chap. XVI.).

Detection of Carnaüba Wax.—Considerable quantities of carnaüba wax may be detected qualitatively by the refractometric test and the chloroform test (see p. 756). The best preliminary method, however, is, in the absence of mineral waxes and insect wax, *Weinwurm's* test, as I have ascertained by experiments in my laboratory. According to *Berg*, mixtures of beeswax and carnaüba wax commence to melt at 68°-70° C., and are not completely melted at 79°-80° C. From the "ratio number" of the wax conclusions can be drawn as to the presence of carnaüba wax, provided other adulterants, which influence the ratio number in the same manner, be absent. If they be present, a thorough examination of the neutral esters is required. The quantitative determination of carnaüba wax in beeswax is a very difficult problem, and can only be solved with sufficient accuracy by an exhaustive examination of both the free and combined fatty acids,

and of the alcohols by the acetylating and potash-lime processes, described Vol. I. Chap. IX.

Detection of Insect Wax.—As a preliminary test for the detection of insect wax, in the absence of mineral waxes and carnaüba wax, the *Weinwurm* test can be recommended. If insect wax be the only adulterant, then its presence will be detected by an abnormally high "ratio number." It has been pointed out above (p. 768) that in a sample so adulterated the iodine value 11·5 was found. As insect wax ought to have lowered the iodine value of the adulterated sample considerably, some other foreign substance must have been added (perilla oil ?). It is evident that the detection of insect wax offers difficulties similar to those experienced in the search for carnaüba wax. In doubtful cases the problem can only be solved by a thorough examination of the neutral esters.

Detection of Wool Fat and Wool Wax.—The presence of wool fat or wool wax is best recognised by testing the alcohols for cholesterol or isocholesterol. As I have shown (Vol. I. Chap. IX.) that cholesterol can be recovered almost completely from the potash-lime used in *Buisine's* process, the safest plan is to convert the alcohols into acids, and to examine the extracted hydrocarbons for cholesterol.

In addition to the adulterants enumerated above, there would also have to be considered as a possible adulterant *Montanwax* (see Vol. III. Chap. XVI.). Methods for its detection have not yet been worked out (cp. below).

The author applies in a thorough examination of a sample of beeswax, the following tests in the order enumerated here :—

Acid value, saponification value, specific gravity, melting point; percentage of unsaponifiable matter, iodine value, determination of glycerin, Weinwurm test, extraction with alcohol and examination of the extracted fatty acids, percentage of fatty acids yielding respectively easily soluble and sparingly soluble soaps (by a method applied first in the examination of wool wax ;[1] see Vol. I. Chap. XI.).

The **unsaponifiable matter** is then further examined for *melting point, increase on acetylation, appearance of the acetylated mass in the hot, saponification value of the acetate,* and, if need be, the alcohols should be converted into fatty acids.

Each portion of the **fatty acids** isolated from the easily soluble and sparingly soluble soaps is examined separately for *melting point* and *molecular weight.* The quantity of fatty acids isolated from the *sparingly* soluble soaps is, as a rule, contaminated with stearic acid, etc., and cannot be calculated direct as cerotic acid ; it is therefore advisable to treat these fatty acids with 80 per cent alcohol (see p. 770), in order to remove acids of a lower melting point than that of cerotic. Any "montanic" acid due to the presence of montanwax, as also carnaübic acid from carnaüba wax, would be found with the "cerotic" acid. Nor should the whole amount of "cerotic" acid be calculated

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 134 ; 1896, 14.

to beeswax, unless the absence of insect wax has been ascertained. By applying these tests in a systematic fashion, and by calculating that composition which satisfies best the analytical data, the many errors inherent to the methods can be eliminated to a very large extent, so that the final results may approximate to the true composition within 3 to 5 per cent.

If the acid value and saponification value found in the actual sample be diminished by those amounts which are due to added free fatty acids and saponifiable substances respectively, the calculated acid and saponification values may, as a rule, be looked upon as due to beeswax only. If a "normal" beeswax had been used in the production of the sample, the ratio of acid value to saponification value will then be about 20 : 95 for a crude wax, and about 25 : 95 for a bleached wax. In case a sample consist of Indian or Chinese beeswax only (see table, p. 766), its abnormal acid and saponification values will define its origin, if no adulterant can be detected. In that case, confirmation may be found in the consistence, these waxes being much softer than African waxes; they are further characterised by a peculiar aromatic odour. It would be impossible to condemn these waxes, inasmuch as they are the genuine secretion of the bee (see above), although not that of *Apis mellifica*. This point deserves the serious attention of the analyst, as the quantities of beeswax exported from India alone are not inconsiderable. This may be gathered from the following table[1]:—

Quantity of Beeswax exported from the Whole of India

	Cwts.
1878–79	3311
1880–81	6592
1885–86	5635
1887–88	5989
1888–89	4573
1889–90	4222
1890–91	6514
1891–92	5814
1892–93	4667
1893–94	5816
1894–95	7487
1895–96	5882
1896–97	3142
1897–98	3537
1898–99	4846
1899–1900	5787
1900–1	5059
1901–2	4139
1902–3	4481

The production of 1902-3 came from Bengal (3020 cwts.), Bombay (762), Madras (427), Burma (230), and Sind (42 cwts.);

[1] D. Hooper, *Agricultural Ledger*, Calcutta, 1904, No. 7.

and was exported to Straits (2062 cwts.), United Kingdom (1313), Germany (534), Ceylon (312), France (176), United States (67),[1] Java, Belgium, and Mauritius (17 cwts.). These beeswaxes differ from the wax of the domesticated bee by containing a smaller amount of free cerotic acid and hydrocarbons, and inferentially by a larger proportion of "myricin." But as they are used in industry, can be bleached successfully, and enter largely into the composition of candles, the greatest caution is required in judging a beeswax which consists of a mixture of "normal" and "abnormal" beeswaxes. To emphasise this point, the following table, due to *Buchner*,[2] may be reproduced :—

Calculated Acid and Saponification Values of Mixed "Normal" and "Abnormal" (Ghedda) Beeswaxes

Ghedda Wax. Per cent.	"Normal" Beeswax. Per cent.	Acid Value.	Saponification Value.
10	90	18·5	94·8
20	80	17·6	95·2
30	70	15·5	94·5
40	60	14·1	94·4
50	50	12·6	94·2
60	40	11·1	94·1
70	30	9·7	94·0
80	20	8·2	93·8
90	10	6·7	93·7

It will thus be seen that if such mixtures be under examination the analysis of beeswax offers the greatest difficulties. In such a case only the rigorous elimination of all possible adulterants by an exhaustive search can lead to decision.

The chief uses of beeswax are for making candles (Russia alone consumes about 6500 tons per annum), wax polishes, and modelling wax.[3] Smaller quantities are employed in the manufacture of cosmetics, cerates, ointments, encaustic paints, and for galvanoplastic purposes.

Reliable statistics as to the world's production are not available, but it may be stated that the import of beeswax into Germany in the year 1902 amounted to 1421 tons.

[1] The total import of beeswax into the United States amounted in 1905-6 and 1906-7 to 5228 and 8200 cwts. respectively.

[2] Buchner, *Chem. Zeit.* 1906, No. 43 ; *Chem. Zeit.* 1908, No. 7.

[3] For modelling flowers, fruits, illustrations of botanical specimens, and finest works of art pure beeswax is used, or at most a small quantity of lard is added, in order to make the wax more pliable. For larger models stearine or rosin, or both, are admixed with bleached wax in definite proportions. Cheap modelling waxes now made for purposes of instruction contain considerable amounts of paraffin wax, and also of sulphur.

Isolated data are the following:—France produces about 2500 tons of beeswax, Russia about 2400 tons, Madagascar from 150 to 200 tons, and Algeria from 100 to 150 tons per annum.

The value of the total export of beeswax from the Gambia Protectorate and colony was £1787 in 1906, and that from Abyssinia £46,530.

RUMP GLAND WAX

French—*Cire des glandes anales des oiseaux.*
German—*Bürzeldrüsenwachs.* Italian—*Cera di codrione degli uccelli.*

This wax occurs in the rump glands of birds, together with animal fat. The following characteristics of the wax have been given by *Röhmann*[1]:—

Acid value	136-175
Iodine value	15·5-26·5

The wax contains up to 43·5 per cent of octodecyl alcohol. Cholesterol is absent. The saturated acids are stated to exhibit optical activity.

SPERMACETI (CETIN)

French—*Blanc de baleine, Cétine.* German—*Walrat.*
Italian—*Spermaceto.*

For table of characteristics see p. 780.

Spermaceti (cetin) occurs chiefly in the head cavities and in the blubber of the sperm whale, *Physeter macrocephalus* (cp. p. 724), and the bottlenose whale, *Hyperoödon rostratus*; it has been also found in somewhat smaller quantities in other *cetacea*; it constitutes the solid portion of dolphin oil (p. 388) and of shark liver oil. The mode of preparing crude spermaceti has been described above, p. 725. Crude sperm oil yields about 11 per cent of spermaceti. The crude spermaceti is melted and boiled two to three hours with a dilute caustic soda lye, containing about 2·5 per cent of caustic soda, and finally washed with water till free from alkali. The clarified oil is then drawn off into flat tin moulds, in which the mass is allowed to crystallise. The cakes are broken up and comminuted to powder, which is pressed in bags in a hydraulic press, first in the cold and then in the hot.

Refined spermaceti forms lustrous, white, translucent, tasteless, and odourless masses with a broad leafy crystalline structure; it is so brittle that it can be rubbed to powder. In the melted state it leaves a grease-spot on paper. It is insoluble in cold 90 per cent alcohol, and sparingly soluble in 96 per cent alcohol; it dissolves, however, easily in boiling alcohol (1 part in 40 parts). On cooling, the bulk separates in a crystalline condition. Spermaceti is readily soluble in ether, chloroform, and carbon bisulphide.

[1] *Zeit. f. die gesamte Biochemie*, 1904, 111.

Physical and Chemical Characteristics of Spermaceti

Specific Gravity.			Solidifying Point.		Melting Point.[1]		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·960	Dieterich	43·4-44·2	Rüdorff	43·5-44·1	Rüdorff	128	Allen
,,	0·905-0·945	Kebler	48	Allen	49	Allen	125·8-134·6	Kebler
60 (water at 15·5=1)	0·8358	Allen	42-47	Kebler	45	Barfoed	130·6-131·4	Henriques
					42-44·5	Kebler	122·7-130·1	Lewkowitsch
98-99	0·8086-0·812	Allen						
(water at 15·5=1)	0·8082-0·816	Kebler	41-45·7	Dunlop	41-46	Dunlop	120·6-129	Dunlop

Physical and Chemical Characteristics of Spermaceti—continued

Alcohols.[2]		Fatty Acids.		Iodine Value.	
Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
51·41	Lewkowitsch	53·45	Lewkowitsch	3·8	Lewkowitsch
51·56-54·27	Dunlop	49·78-50·58	Dunlop		

[1] The melting point of a specimen of spermaceti melting at 42° C. was raised to 43·5° C., by crystallising twice from alcohol, and by subsequent recrystallisation from ether 5 times to 48·5° C. (Fendler, *Chem. Zeit.* 1905, 555).

[2] Melting point of the alcohols 46·7° C. (*Lewkowitsch*); 45° C. (Fendler, *Chem. Zeit.* 1905, 555); 45·5° to 48° C. (*Dunlop*). The iodine numbers of the alcohols prepared by *Dunlop* varied from 2·98 to 6·35.

Chemically, spermaceti consists chiefly of cetin,[1] *i.e.* cetyl palmitate. Since the saponification value of pure cetin is 116·9, it is evident that other esters must occur in spermaceti. This is confirmed indirectly by the percentage increase on acetylating the alcohols (see Vol. I. Chap. IX.). The statement[2] that spermaceti contains also glycerides of lauric, myristic, and stearic acids as normal constituents requires confirmation. *Lewkowitsch*[3] found in a commercial sample of the saponification value 122·3, the acetyl value 2·63; this would point to the presence of a small amount of free alcohols. By crystallisation from alcohol pure cetin is obtained.

On examining *commercial* samples, the author found iodine absorptions of 3·52 to 4·09, no doubt owing to small quantities of sperm oil adhering to the spermaceti. The higher iodine values found by *Dunlop*, viz. 5·3-9·33, must be due to some sperm oil having remained behind; this is confirmed by the exceedingly low melting points of the fatty acids which *Dunlop* found, viz. 32 to 40. If other iodine-absorbing impurities (tallow) are absent, the proportion of sperm oil may be calculated, adopting 82·5 as its iodine value.

The esters in spermaceti are readily saponified by boiling with alcoholic potash; on diluting the alcoholic solution with water, cetyl alcohol is precipitated.

Spermaceti cannot be easily adulterated, as any foreign substance causes it to lose its physical characters, such as transparency and crystalline structure. Genuine samples of commercial spermaceti contain small quantities only of free fatty acids. Thus *Lewkowitsch* found in a commercial sample the acid value 1·35; *Kebler*, in the examination of twelve samples of spermaceti acid, values ranging from 0·09 to 0·47; and *Dunlop*, 0·20 to 0·48.

A higher acid value of a sample would indicate the presence of *stearic acid* or *beeswax*, a high iodine value that of *tallow*. These substances would also be pointed out by abnormal saponification values. They, as also *paraffin wax*, may be identified by the methods described under "Beeswax."

A rapid process for the detection of *stearic acid*[4] is to melt the sample in a porcelain basin, and to stir it well with a few c.c. of ammonia. After cooling, the solidified cake is removed and the aqueous solution acidified, when stearic acid separates. The presence of even 1 per cent of stearic acid may be thus ascertained.

Spermaceti is employed in the manufacture of sperm candles, some kinds of "beeswax" candles, cerates (see Vol. III. Chap. XV.), and for cosmetic purposes.[5] The alcohols obtained from spermaceti are said to form a useful basis for ointments.[6]

[1] The requirements of the U.S. Pharmacopœia appear to correspond rather with the numbers calculated for cetin than those ascertained hitherto for spermaceti; cp. L. Kebler, *Journ. Soc. Chem. Ind.* 1896, 206.

[2] Heintz, *Liebig's Annalen*, 92. 291.

[3] *Analyst*, 1899, 321.

[4] *Les Corps gras industriels*, 13. 207.

[5] *Zeit. f. ang. Chem.* 1905, 1760.

[6] A mixture of these alcohols with vaseline is sold under the fancy name "Cetosan" (Blatz, *Pharm. Zentralh.* 1908, 537).

INSECT WAX, CHINESE WAX

French—*Cire d'insectes, Cire de Chine.* German—*Insektenwachs, Chinesisches Wachs.* Italian—*Cera d' insetti.*

For table of characteristics see p. 783.

Insect wax is the secretion of an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood.

The larvæ of the insect appear early in the spring on the bark, boughs, and twigs of *Ligustrum lucidum*, Ait. (the "evergreen" tree growing in the Chien-Chang valley, Western China, near the Thibetan frontier), in the form of numerous brown pea-shaped scales. These scales are gathered by the natives about the end of April, wrapped carefully in packages (each containing about 1 lb.), so as to protect the larvæ from the heat whilst these packages are being carried to Chia-ting, the centre of the insect wax industry, a distance of about 200 miles from the Chien-Chang valley. (In order to prevent the premature development of the larvæ, the packages must be kept as cool as possible and, therefore, the carriers only travel by night.) Each package is subdivided into smaller packages, wrapped in leaves, and suspended under the branches of a species of ash (most likely *Fraxinus chinensis*), after holes have been made in the leaves which cover the larvæ. On emerging from the scales, the insects creep up the branches to the leaves of the tree, among which they remain thirteen days; they then descend to the branches and twigs, where the insect wax is secreted. The first appearance of the wax on the undersides of the boughs and twigs resembles snow; it gradually spreads over the whole branch to the depth of about a quarter of an inch. Three months after placing the insects on the tree the branches are cut off, and as much wax as possible is removed by hand. In order to recover a further quantity the branches are boiled with water. The larvæ are thereby destroyed, and hence fresh scales must be brought the following year for another crop of wax. One pound of scales is stated to produce four to five pounds of wax (*Hosie*).

The annual production of insect wax varies greatly with climatic conditions, as wind and rain act destructively on the insects.

Insect wax has a yellowish-white colour; it is odourless and tasteless, has a lustrous appearance and a crystalline structure, resembling in these respects spermaceti; it is, however, more fibrous and considerably harder, and can be powdered more easily.

This wax is very slightly soluble in alcohol and ether, but easily soluble in benzene, from which it can be obtained in a crystalline form. It consists chiefly of ceryl cerotate, $C_{26}H_{53} \cdot C_{26}H_{51}O_2$, which can be readily isolated from the wax by repeated crystallisation from petroleum ether (boiling point 115°-135° C.). Since the theoretical saponification value of ceryl cerotate is 73·8, other esters

Physical and Chemical Characteristics of Insect Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Fatty Acids.		Alcohols.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·970	Allen	80·5-81	Allen	80·5-81	Allen	93	Henriques	51·54[1]	Lewko-witsch	49·51	Lewko-witsch	1·4	Lewko-witsch
99 (water 15·5 = 1)	0·810	,,			81·5-83	Henriques	80·5	,,						
							91·65	Lewkowitsch						
							80·4	,,						

[1] Melting point of the fatty acids 92·2° C. (*Lewkowitsch*).

are evidently admixed with the ceryl cerotate, as the saponification values of commercial samples are considerably higher. Owing to the separation of potassium cerotate during saponification and titration, low saponification values were found by earlier observers; such lower numbers are omitted here. A commercial sample of Chinese wax examined by the author absorbed 1·4 per cent of iodine. Another sample had the acid value 1·5. In the *Weinwurm* test (see p. 772) Chinese wax behaves like a beeswax adulterated with paraffin wax (*Lewkowitsch*).

Insect wax is used in China and Japan for making candles, for polishing furniture and leather, and as a sizing material for paper, silk, and cotton goods. On account of its extensive use in China and Japan it is not largely exported to Europe.[1]

Psylla Wax [2]

This wax is secreted by *Psylla alni*, an aphide living on the leaves of *Alnus incana*. It is obtained by extracting the insects first with hot ether, in order to remove glycerides, and finally with hot chloroform.

The wax is insoluble in hot ether, and only sparingly soluble in cold chloroform, but readily soluble in hot chloroform and in benzene. It crystallises in needles of silky lustre, melting at 96° C.

Psylla wax is the psyllostearylic ester of psyllostearyl alcohol (see Vol. I. Chap. III.). The hydrolysis of the wax is stated to be effected less expeditiously by alcoholic potash than by hydrobromic acid.[3]

Wax from Tuberculosis Bacilli

French—*Cire de bacille tuberculeux.* German—*Tuberkelbacillenwachs.* Italian—*Cera di tubercoli.*

On extracting dried tuberculosis bacilli with chloroform, *Kresling* [4] obtained a fatty substance consisting, according to his statements, of:—free fatty acid, 14·38 per cent; neutral fats and fatty acid esters, 77·25 per cent; lecithin, 0·16 per cent; water-soluble substances, 0·73 per cent. From the "fatty acid esters," 31·9 per cent of alcohols melting at 43·5° C. were obtained. The total fatty matter had the following characteristics:—

Melting point	46° C.
Acid value	23·08
Reichert-Meissl value	2·00
Fatty acids + unsaponifiable	74·24 per cent.
Saponification value	60·70
Iodine value	9·92

[1] *Journ. Soc. Chem. Ind.* 1897, 685.

[2] Sundwick, *Zeit. f. phys. Chem.* 1901 (32), 355. [3] *Ibid.* 1908 (54), 255.

[4] "Ueber die Fettsubstanz der Tuberkelbacillen," *Centralbl. f. Bakteriologie*, Abt. i. 1901, xxx. 897.

The fatty substance seems to be a wax,[1] which is only saponified with great difficulty; for a similar preparation obtained by *Bullock and Macleod* by extracting dry tubercle bacilli with *Aronson's* mixture (alcohol and ether containing 1 per cent of hydrochloric acid), furnished, after saponification with sodium alcoholate, a substance which on examination by *Lewkowitsch*[2] gave the following numbers:—

Iodine value	9·39
Saponification value	49·40
Melting point	44·4° C.
Increase of weight on acetylating	1·2 per cent.
Saponification value of acetylated product	69·0

These numbers show that a considerable amount of the wax had escaped saponification.

The manufacture of the wax ("fatty substance") from tuberculosis bacilli and other micro-organism, especially from *Streptothrix leproides*, and its employment for medicinal purposes[3] has been patented by *Kalle and Co.*[4]

[1] Cp. Ritchie, *Journ. Path. and Bact.* 1905, 334.

[2] "Chemical Constitution of the Tubercle Bacillus," by W. Bullock and J. J. R. Macleod, *Journal of Hygiene*, vol. iv. 1904, p. 7.

[3] Cp. Deycke (Pasha) and Reschad (Bey), *Deutsch. medic. Wochenschr.* 1907, 89.

[4] English patent 26,077, 1906; German patents 193,883, 199,200; English patent 27,383, 1907; German patent 201,989. An addition to German patent 199,200 claims as solvents (for the extraction of the "fatty substance") benzaldehyde, benzyl alcohol, salicyl aldehyde, cinnamic aldehyde, and benzoyl chloride. Cp. also *Zeit. f. angew. Chem.* 1909, 102.

Lesser Known Animal Waxes

Wax from	French.	German.	Italian.	1 Number of Samples.	2 Specific Gravity at 15° C.	3 Melting Point. °C.	4 Butyro-refractometer "Degrees" observed at 84° C., calculated to 40° C.	5 Acid Value.	6 Saponification Value.	7 Difference, 5-4.	8 "Ratio Number."	8 Iodine Value.	9 c.c. $\frac{1}{10}$ norm. KOH required for Acids soluble in 80 per cent Alcohol.	10 Hydrocarbons. Per cent.	Observer.
Bumble bee[1] . from Bombus terrestris, B. muscarum, B. lapidarius — Max.	Cire de bourdon	Hummelbienenwachs	Cera di calabrone		...	63·0	51·6	19·39	95·90	76·65	4·00	16·10	9·18	...	Berg
Mean				19	...	62·0	50·0-51·0	19·0-19·2	95·0-95·5	76·0-76·5	3·95-4·0	15·8-15·9	5·0-7·0	...	Berg
Min.					...	62·0	49·5	18·41	92·12	73·71	3·93	15·76	4·92	...	Berg
,, ,, . .				...	0·973	...	...	7·8	48·3	40·5	5·2	...	...	25·1	Ahrens a Hett
Cicade wax—I. . .	Cire de cicade	Cicadenwachs	Cera di cicale	...	0·965	...	...	7·8	95·9	88·1	11·29	...	...	10·6	,,
,, ,, II. . .				...	0·965	...	...	7·3	97·95	90·65	12·41	...	...	8·2	,,
Ceroplastes ceriferus[2]— Expressed . .				...	1·04	60									,,
Extracted . .				...	...	55									
Ceroplastes rubeus— Expressed . .				...	1·03 at 23° C.	60									,,
Extracted . .				...	...	55									

Cochineal wax from *Coccus cacti* consists of cocceryl coccerate to an extent of from 0·5 per cent (in Zacatille cochineal) to 4·2 per cent (in Granilla cochineal).

[1] This wax has a very unpleasant smell, which it has not yet been possible to remove ; it cannot, therefore, be used as an admixture to genuine beeswax (R. Berg, *Chem. Zeit.* 1907, 538). *Sundwick* (Hoppe Seyler's *Zeit. f. physiolog. Chem.* 1898, 56 ; 1907 (55), 365) detected psyllostearyl alcohol amongst the alcoholic constituents of bumble wax.

[2] This wax is known in commerce as "Arjun wax." The "Mission forestière de l'Afrique occidentale française" found the Ceroplastus insect on two species of acacia, which are widely distributed on the banks of the Senegal river.

APPENDIX

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Under the head of bleaching by exposure to light would also fall the process of bleaching oils by exposure to the *Cooper-Hewitt* mercury lamp. *Genthe*[1] bleaches linseed oils in this manner for purposes of varnish manufacture (cp. p. 49); he also prepares "boiled oil" by exposing raw linseed oil to the ultra-violet light of an "uviol" lamp (cp. Vol. III. "Boiled Oils" and "Oxidised Oils from Drying Oils").

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The mixed fatty acids from a specimen of perilla oil (Jap. *Eno-abura*), recently examined by *Kametaka*, yielded in the bromide test (see Vol. I. Chap. VIII.) a white voluminous precipitate, which showed under the microscope no crystalline structure, but consisted of oily drops. The brominated product contained 62·61 per cent of bromine and melted at 181° C.

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A specimen of fresh tung oil (from Echizen) pressed in the cold had the iodine value 161·3 (*Kametaka*). After keeping the oil in an ordinary stoppered bottle for eleven months the iodine value had fallen to 150.

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The characteristic smell of tung oil seems to develop whilst the oil is in transit to Europe, for oil expressed from fresh seeds on the spot has by no means an unpleasant smell.

The cake obtained in the preparation of tung oil used to be credited also with poisonous properties, and it was applied to the land as a fertiliser; but since the Japanese now employ higher temperatures than they did formerly in expressing the oil, the cake has been found to be non-poisonous. Probably the seeds contain a cyanogenetic glucoside and an enzyme which is rendered innocuous by the elevated temperature.[2]

[1] German patent 195,663.

[2] Cp. Divers, *Journ. Soc. Chem. Ind.* 1908, 433.

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The mixed fatty acids of Kaya oil contain stearic acid and linolic acid (*Kametaka* [1]).

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The botanical name of the "Jequié" Manihot (a tree occurring in the south-east of Bahia, in the neighbourhood of the town of Jequié) is *Manihot dichotoma*, Ule. The oil is expressed from the seeds, and is stated to be used as a substitute for linseed oil.

Other indiarubber-yielding species of *Manihot* are :—*M. heptaphylla*, Ule (Sao Francisco Manihot) ; *M. pianhyensis*, Ule (Pianhy Manihot) ; *M. violacea*, Müll. Arg. ; *Hotnima Teissonieri*, A. Chev. (*M. Teissonieri*, A. Chev.).

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MILLET SEED OIL

French—*Huile de millet.* German—*Hirsenöl.*
Italian—*Olio di miglio ; Olio di panico.*

This oil was prepared by *Fabris and Settimj* [2] by extraction of the powdered grains of millet (*Panicum italicum*) with ether. Thus 3·5 per cent of a turbid oil was obtained from which mucilaginous substances separated on standing. The filtered oil is brownish-yellow ; its odour resembles that of oils from cereals. It is insoluble in cold absolute alcohol, but dissolves in boiling absolute alcohol.

The following characteristics were determined by *Fabris and Settimj* :—

Oil—	
Specific gravity at 15° C.	0·9275
Solidifying point	−6° to −7° C.
Saponification value	183·8
Iodine value	130·4
Butyro-refractometer "degrees" at 25° C.	70
Maumené test	67·5° C.
Insoluble Fatty Acids—	
Fatty acids + unsaponifiable	95·5 per cent
Solidifying point	19° to 20° C.
Melting point	26° to 27° C.
Iodine value	134·3
Iodine value of the liquid fatty acids	146·3

The mixed fatty acids consisted of 84·5 per cent of liquid and 15·5 per cent of solid fatty acids. With regard to "Millet Oil Acid" see Vol. I. Chap. III.

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A monograph on *Argemone mexicana* has been published recently by *D. Hooper*.[3]

[1] *Journ. of the College of Science*, Tokyo, xxv. Art. 4, 1908.
[2] *Atti del VI. Congresso internaz. di chimica applicata*, Roma, 1907, v. 754.
[3] *Agricultural Ledger*, 1907, No. 5 (1908).

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STRAWBERRY SEED OIL

Kochs[1] examined a specimen of oil (from *Fragaria vesca*), the characteristics of which differ widely from those given p. 113. Thus the specific gravity is 0·974, the iodine value 72·8, and the *Reichert-Meissl* value 13·42. From these numbers it would appear, as *Kochs* himself stated, that a partial oxidation (thickening) of the oil took place whilst the seeds were ground up to pulp. At the same time considerable hydrolysis must have occurred, as the sample had the high acid value 56.

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RED CURRANT SEED OIL

French—*Huile de groseille.* German—*Johannisbeersamenöl.*
Italian—*Olio di ribes.*

The dried seeds of the currant, *Ribes rubrum*, L., contain 16·9 per cent of an oil of yellowish-brown colour and of pleasant odour. The oil examined by *Kochs*[2] had the acid value 5·6, and gave the following characteristics :—

Oil—	
Specific gravity at 15° C.	0·9120
Solidifying point	below −17·5° C.
Saponification value	171·3 (!!)
Iodine value	152·5
Reichert-Meissl value	0·77
Butyro-refractometer "degrees" at 40° C.	62
Unsaponifiable	2·31 per cent.
Fatty Acids—	
Melting point (capillary tube)	−20° C.
Neutralisation value	211
Iodine value	159·5

Kržižan[3] examined two specimens of Italian and of Bohemian origin respectively, with the following results :—

	Italian Oil.	Bohemian Oil.
Oil—		
Specific gravity at 15° C.	0·9265	0·9303
Saponification value	189·9	186·9
Iodine value	172·3	175·9
Mixed Insoluble Fatty Acids—		
Specific gravity at 15° C.	0·9117	...
Neutralisation value	196·3	...
Iodine value	178·7	...
Acetyl value	13·2	...
Liquid Fatty Acids—		
Neutralisation value	199·9	200·6
Iodine value	187·8	193·0

[1] *Jahresb. d. Versuchs. d. k. Gärtnerlehranst. für* 1906-1907, Dahlem. [2] *Ibid.*
[3] *Chem. Revue*, 1909, 1.

The Italian oil gave off sulphuretted hydrogen on decomposing the saponified oil with mineral acid, hence the oil gave a fictitious *Reichert-Meissl* value (1·1). The Bohemian oil was free from sulphur. The Italian oil contains stearic and palmitic acids (about 5 per cent), large quantities of linolic acid, and smaller quantities of oleic and linolenic acids.

The oil dries, on exposure to the air at a temperature of 50° C., in seven hours to a dry, almost colourless skin (*Kochs*). The increase in weight on drying at the ordinary temperature was 8·78 per cent (*Kržižan*).

HAWTHORN SEED OIL, HIP OIL

French—*Huile d'églantier.* German—*Hagebuttensamenöl.*
Italian—*Olio di rosa canina.*

The seeds of the berries of *Cratægus oxyacantha*, *Rosa canina*, etc. (known as hips), contain 9·63 per cent of an oil of pleasant smell, and of yellow to orange-yellow colour. The oil examined by *Kochs*[1] had the acid value 4·2, and gave the following characteristics :—

Oil—

Specific gravity at 50° C.	0·9161
Solidifying point	below −17·5° C.
Saponification value	172·8
Iodine value	152·8
Reichert-Meissl value	0·44
Unsaponifiable matter	2·62 per cent
Butyro-refractometer "degrees" at 40° C.	67

Fatty Acids—

Neutralisation value	202·9
Iodine value	174·3

On exposure to the atmosphere at a temperature of 50° C. the oil dried after seven hours to a hard, almost colourless skin; at the ordinary temperature it thickened after seven days, and was dry after ten days.

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The "tannoom seeds" from *Chrozophora verbascifolia* yield 35 per cent of a thick oil, which the Bedouins of Arabia use in place of ghee. The oil had the saponification value 200·2, the iodine value 137·0. The insoluble fatty acids had the "titer test" 30·5° C. The acid value of the specimen examined by *Hooper*[2] was 33.

The seeds of *Lawsonia alba*, Lamk. (the henna plant of Western Asia, which is found wild or cultivated throughout India), contain 10·48 per cent

[1] *Jahresb. d. Versuchs. d. k. Gärtnerlehranst. für* 1906-1907, Dahlem.
[2] *Annual Report, Indian Museum*, 1907-1908, p. 13.

of an oil which solidifies at 25·5° C. It has the iodine value 121·63. The oil is not likely to become a commercial product.

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Quite recently the attempts to ship soja beans to this country and to express the oil have been renewed, and this time successfully. Very considerable quantities of both beans and oil are already in the English market. It appears that regular imports from China may be expected in the future.

Kametaka obtained on oxidising a specimen of soja bean oil, dihydroxystearic and sativic acids. On brominating the mixed fatty acid a bromo-derivative, melting at 110° C., was obtained.

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Hooper[1] gives the following characteristics for the oil from *Cucurbita maxima*, the "squashed gourd" of India :—

Oil—	
Specific gravity at 15° C.	0·919 ; 0·926
Saponification value	194·9 ; 197·1
Iodine value	88·7 (?) ; 133·4
Reichert-Meissl value	0·47 ; 0·67
Fatty Acids—	
Insoluble acids + unsaponifiable	94·3 ; 95·8
Titer test	32° C. ; 38° C.
Acid value	6·38 ; 17·65

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Hooper[2] examined the seeds from the Indian pumpkin ; these yielded 25 per cent of an oil, having the following characteristics :—

Oil—	
Specific gravity at 15° C.	0·926 ; 0·928
Saponification value	195·7 ; 196·2
Iodine value	126·0 ; 129·6
Reichert-Meissl value	0·43 ; 0·52
Fatty Acids—	
Insoluble acids + unsaponifiable	94·97 ; 94·7 per cent.
Titer test	31·0° C. ; 32° C.
Acid value	12·78 ; 10·86

[1] *Annual Report, Indian Museum*, 1907-1908, p. 13. [2] *Ibid.*

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Hooper[1] examined the oil from the seeds of *Cucumis sativus* from India. The following numbers were ascertained :—

Oil—	
Specific gravity at 15° C.	0·924 ; 0·923
Saponification value	195·2 ; 196·9
Iodine value	117·6 ; 118·5
Reichert-Meissl value	0·52
Fatty Acids—	
Insoluble acids + unsaponifiable	94·2 ; 94·6
Titer test	35·5° C.
Acid value	11·5

Hooper[2] examined the oil from the colocynth seeds of Baluchistan (*Citrullus colocynthis*), which yielded 17·8 per cent of oil. The following characteristics were ascertained :—

Oil—	
Saponification value	202·9
Iodine value	129·3
Fatty Acids—	
Insoluble acids + unsaponifiable	92·2 per cent.
Titer test	29° C.
Acid value	5·9

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Heiduschka and Gloth[3] were unable to detect stigmasterol in the unsaponifiable matter of cotton seed oil, they having obtained only dibromo-derivatives of the acetylated alcohols. With regard to their statement that cotton seed phytosterol is probably an individual substance cp. p. 161.

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Hooper[4] examined specimens of highly acid Luffa seed oil with the following results :—

Oil—	
Specific gravity at 15° C.	0·921-0·926
Saponification value	193·0-195·8
Reichert-Meissl value	0·49-0·52

[1] *Annual Report, Indian Museum*, 1907-1908, p. 13. [2] *Ibid.*
[3] *Pharm. Zentr.* 1908 (49), 863.
[4] *Annual Report, Indian Museum*, 1907-1908, p. 15.

Fatty Acids—

Insoluble acids + unsaponifiable	93·5-94·2
Titer test	34°-35° C.
Acid value	33·0-36·4

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The seeds of *Cochlospermum Gossypium*, a tree occurring in the dry parts of North India, and characteristic of the hottest, driest, and stoniest slopes, contain 14·25 per cent of oil, for which *D. Hooper*[1] ascertained the following characteristics :—

Saponification value	186·29
Iodine value	95·97
Reichert-Meissl value	0·19
Insoluble fatty acids + unsaponifiable	95·19 per cent.
Acid value	14·24

The tree has been suggested as a source of "silk-cotton" (like "Kapok").

SPINDLE TREE OIL

French—*Huile de bonnet de prêtre.* German—*Pfaffenhütchenöl, Spillbaumöl.* Italian—*Olio di fusaggine.*

Spindle tree oil was prepared by *Kochs*[2] from the arillus and the seeds of the spindle tree, *Evonymus europæa*, L. The yield obtained was 35·2 per cent. The oil had a bright reddish-brown colour, due to the colouring matter of the arillus having been extracted together with the oil; hence the unsaponifiable matter was very high. The acid value of the specimen examined by *Kochs* was 84. The oil had the following characteristics :—

Oil—

Specific gravity at 15° C.	0·9390
Solidifying point	−10° C.
Saponification value	230·1
Reichert-Meissl value	35·31
Butyro-refractometer "degrees" at 40° C.	52
Unsaponifiable matter	5·83 per cent.

Fatty Acids—

Melting point—commences to melt at	38° C.
,, ,, completely melted at	70° C.
Iodine value	105·3
Neutralisation value	223·6

The exceedingly high saponification and *Reichert-Meissl* values would

[1] *The Agricultural Ledger*, 1906, No. 5, Calcutta.
[2] *Jahresb. d. Versuchs. d. k. Gärtnerlehranst. für* 1906-1907, Dahlem.

seem to confirm the statement (Vol. I. Chap. III.) that the oil contains acetic acid in the form of triacetin. In view of the extraordinarily high saponification and *Reichert-Meissl* values, which suggest the employment of this oil as a butter adulterant, a more exhaustive examination of the oil is required.

TOMATO SEED OIL

Tomato seeds are obtained as a by-product in the manufacture of tomato pulp. In view of the large quantities that are obtainable, and in view of the fact that the seeds contain 17·3 per cent of oil, the commercial production of this oil may be expected. The following characteristics, which differ widely (especially as regards the *Reichert-Meissl* value) from those given by *Battaglia*, were ascertained by *J. Kochs*[1] :—

Oil—	
Specific gravity	0·920
Solidifying point	below −12° C.
Saponification value	183·6
Iodine value	117·8
Reichert-Meissl value	0·22
Unsaponifiable	2·68 per cent.
Butyro-refractometer "degrees" at 40° C.	63
Fatty Acids—	
Melting point (capillary tube)	26° to 29° C.
Neutralisation value	199·5
Iodine value	129·6

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With regard to the alleged toxic effect observed occasionally after feeding cattle with arachis cake, compare *Benecke*,[2] *Krüger*,[3] *Mooser*,[4] *Lewkowitsch*,[5] *Hefter*.[6]

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The seeds of *Thea sinensis*, L., are round, and have a diameter of about 1 cm. The examination of kernels obtained from Tokyo and Uji plants respectively gave the following results :—Moisture, 15·60 per cent ; 6·46 per cent. Oil, 23·9 per cent ; 26·23 per cent. Ash, 2·6 per cent ; 2·5 per cent. The expressed oil from the Tokyo seed was an orange-yellow liquid, of somewhat unpleasant odour and bitter taste ; it had the acid value 0·74.

The following characteristics were ascertained by *Tsujimoto*[7] :—

[1] *Jahresb. d. Versuchs. d. k. Gärtnerlehranst. für* 1906-1907, Dahlem.
[2] *Landw. Versuch.-Station*, 34, 145. [3] *Chem. Zeit.* 1906, 999.
[4] *Landw. Versuch.-Station*, 1904, 331. [5] *Journ. Soc. Chem. Ind.* 1908, 430.
[6] *Seifensieder Zeit.* 1908, 1277. [7] *Chem. Revue*, 1908, 224.

Oil—

Specific gravity at 15° C.	0·9178
Solidifying point	−10° C.
Saponification value	191·9
Iodine value	90·42
Reichert-Meissl value	0·66
Refractive index at 20° C.	1·4707

Fatty Acids—

Insoluble acids + unsaponifiable	95·6 per cent.
Specific gravity at 98° C.	0·8445
Melting point	33·5° C.
Neutralisation value	197·6
Mean molecular weight	283·9
Iodine value	92·86

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Olive Oil imported into the United Kingdom (in Metric Tons)

	1902.	1903.	1904.	1905.	1906.	1907.
Algeria	...	...	...	7	0·8	...
Italy	4,617	2,684	2,880	2,820	4,798	...
Spain	11,973	9,543	9,928	4,043	228	...
France	1,482	1,213	1,324	1,422	2,348	...
Greece	639	112	367	114	992	...
Crete	...	277	251	537	2,812	...
Tunis	...	...	...	...	...	15

The exports of "refined" olive oil and of all other grades from Italy in the past three years are given by the Italian Customs authorities as follows:—

Italian Exports of "Refined" Olive Oil

Exported to	Quintals.[1]		
	1905.	1906.	1907.
United States	38,687	71,400	29,188
Austria-Hungary	7,752	22,203	28,998
Germany	5,490	11,132	15,690
Great Britain	4,102	9,432	5,861
Holland	8,403	23,519	12,648
Switzerland	6,936	11,294	7,626
Egypt	4,867	19,285	15,353
Other countries	4,900	8,894	8,536
Totals	81,658	177,172	124,881
Total values	$945,600	$2,051,652	$1,491,122

[1] 1 quintal = 220·46 lb.

Italian Exports of all other Grades of Olive Oil

Exported to	Quintals.[1]		
	1905.	1906.	1907.
Austria-Hungary	18,293	25,834	19,013
France	43,191	116,312	60,766
Germany	11,058	21,222	17,793
Great Britain	22,184	29,737	25,000
Russia	29,765	22,854	26,677
Switzerland	5,668	8,819	7,124
Egypt	1,956	5,810	2,636
United States	52,577	95,258	82,198
Brazil	8,820	12,320	14,495
Argentina	58,256	109,194	90,347
Uruguay	3,893	8,190	9,402
Other countries	17,440	33,032	32,976
Totals	273,101	488,582	388,427
Total values	$6,852,104	$11,787,041	$9,370,801

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LYCOPODIUM OIL

This oil is prepared by extracting lycopodium spores with chloroform. *Rathje*[2] thus obtained 49·2 per cent of a bright yellowish-green oil, having the following characteristics :—

Oil—

Specific gravity	0·93617
Saponification value	195·0
Iodine value	81·0
Reichert-Meissl value	7·3
True acetyl value	44·1
Refractive index	1·4671
Unsaponifiable matter	0·43 per cent.

Fatty Acids—

Fatty acids + unsaponifiable matter	88·0 per cent.
Melting point	39°-40° C.
Neutralisation value	202·0
Mean molecular weight	278·0
Iodine value	91·8
Iodine value of the liquid fatty acids	98·7

The extracted oil had the acid value 18·6. According to *Rathje*, the oil contains "lycopodic acid," 81 per cent; dihydroxystearic ("lycopodium acid"), 3·2 per cent; small quantities of stearic and palmitic (about 1 per cent of each), and about 2 per cent of myristic acid. [It should be pointed out that the proportions of solid acids were determined by *Partheil and Ferié's* (incorrect) lithium-salt method.] The nature of the volatile acids, which must be present in notable quantities, was not investigated.

[1] 1 quintal = 220·46 lb.

[2] *Archiv d. Pharm.* 1908, 699.

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Hooper[1] examined a specimen of "Java almonds" which yielded 34 per cent of oil. The following characteristics of the oil were ascertained :—

Oil—	
Specific gravity at 30·5° C.	0·919
Saponification value	199·3
Iodine value	83·0
Fatty Acids—	
Insoluble acids + unsaponifiable	95·6 per cent.
Titer test	31·5° C.
Acid value	6·5

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SECALE OIL

Fabris and Settimj[2] obtained by extraction 30 per cent of a brownish-yellow oil, which had the characteristics given in the second column of the following table. The third column of the table states the numbers obtained by *Rathje*.[3]

	Fabris and Settimj.	Rathje.
Oil—		
Specific gravity at 15° C.	0·927	0·9250
Solidifying point	−10° C.	...
Saponification value	191·4	178·4-180·2
Iodine value	74·6	73·4-74·5
Reichert-Meissl value	...	0·61-0·67
True acetyl value	...	27·44
Butyro-refractometer "degrees" at 25° C.	65	...
Refractive index	...	1·4685
Maumené test	51° C.	...
Unsaponifiable	...	0·36 per cent
Fatty Acids—		
Insoluble acids + unsaponifiable	98·5 per cent (?)	95·8-96·6
Solidifying point	30°-31° C.	...
Melting point	37°-38° C.	38°-39° C.
Neutralisation value	...	183
Iodine value	75·8	77·2
Iodine value of the liquid fatty acids	104	82·2

The insoluble fatty acids consist, according to *Fabris and Settimj*, of 64 per cent of liquid acids and 46 per cent of solid acids. This agrees much better with the melting point of the mixed fatty acids than does *Rathje's* conclusion that the oil contains 5 per cent of palmitic, 68 per cent of oleic, and 22 per cent of hydroxyoleic acids.

[1] *Annual Report, Indian Museum*, 1907-1908, p. 13.
[2] *Atti del VI. Congresso internaz. di chimica applicata*, Roma, 1907, v. 761.
[3] *Archiv der Pharm.* 1908 (246), 697.

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OLEANDER OIL

French—*Huile de Laurier-rose.* German—*Oleanderöl.*

The seeds of *Nerium oleander*[1] contain 16 per cent of an oil which has the following characteristics :—

Saponification value	202 to 203
Iodine value	88
Reichert-Meissl value	10·26
Unsaponifiable matter	19·5 per cent (!)

TERMINALIA OIL, MYROBALAN OIL

Fatty oils are derived from several species of *Terminalia*, namely, *T. catappa* ("Country almond"), the seeds of which contain 48·3 per cent of oil; *T. belerica*, which yields 25 per cent of "Baheda oil"; *T. chebula*, which yields 36·71 per cent of oil.

The characteristics of the respective oils are given in the following table[2] :—

	T. catappa.	*T. belerica.*	*T. chebula.*
Oil—			
Colour	...	Yellow	Yellowish
Specific gravity at 15° C.	0·9206	0·9168 ; 0·9193	...
Melting point	3·5° C.	11° C. ; 4° C.	...
Saponification value	203·04	205·8 ; 205·3	192·66
Iodine value	81·8	79·04 ; 85·38	87·5
Reichert-Meissl value	...	0·76 ; 0·78	...
Fatty Acids—			
Insoluble acids + unsaponifiable	95·2 per cent	94·2 ; 93·6	96·2
Titer test	42° C.	39° C. ; 38° C.	
Acid value	7·77	2·48 ; 3·97	8·91

The seeds of the "iron wood of Assam" ("Nag Kesm"), from *Mesua ferrea*, yield 41·6 per cent of oil (the kernels alone yield 72·9 per cent). The oil is deep yellow or brown; at the ordinary temperature "stearine" is deposited from the oil. The following characteristics were ascertained[3] :—

Oil—	
Specific gravity at 15° C.	0·9166-0·9359
Melting point	16·5°-26·7° C.
Saponification value	203·7-205·8
Iodine value	88·7-89·1
Reichert-Meissl value	7·7-11·54
Fatty Acids—	
Insoluble acids + unsaponifiable	92·2-94·1 per cent.
Titer test	33·5°-34·5° C.

[1] J. Camo, *Bulletin des scienc. pharmacolog.* 1908, No. 8, p. 442.
[2] D. Hooper, *Annual Report, Indian Museum*, 1907-1908, p. 13. [3] *Ibid.*

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The statement that "the proportion of bromo-compounds no doubt depends on the state of freshness of the sample under examination" is confirmed by the results of some analyses made by *Bull and Johannesen*,[1] who obtained from ten commercial medicinal cod liver oils 27·08-34·92 per cent of ether-insoluble brominated acids.

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Dubovitz [2] found the iodine value of an Italian chrysalis oil 111·5, and that of an oil obtained from the chrysalides from an Hungarian silk works 138·7. The statement made by *Dubovitz* that the oil contains a considerable amount of hydroxylated acids (determined by the faulty method of *Benedikt and Ulzer*) requires confirmation.

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Oil from Carapa procera, D.C. (= Carapa guyanensis)

The author received from the Imperial Institute a considerable quantity of the seeds of "*Carapa guyanensis*." There is some confusion with regard to the botanical origin of these Carapa seeds. The seeds were sent from Sierra Leone as *Carapa guyanensis*, Aubl., apparently following a mistake in Oliver's *Flora of Tropical Africa*. The species founded by *Aublet* was, however, *Carapa guianensis*, and this is confined to the West Indies and South America. It seems, therefore, probable that the nuts sent from Sierra Leone are derived from *Carapa procera*, D. C., of which *C. guyanensis*, Oliv., and *C. guineensis*, A. Juss., are synonyms.

A large proportion of the kernels were mouldy, hence in several lots of nuts, amounting to about 20 lbs. each, the good and bad kernels, as also the shells, were determined quantitatively, with the following result:—

Good kernels	35·5 per cent
Bad kernels	27 ,,
Shells	37·5 ,,

The sound kernels yielded, by extraction with ether, 57·26 per cent of oil.

A large quantity of good kernels were comminuted in the manner simulating the operations on a large scale, and were pressed in the cold in a hydraulic press at a pressure of 150 atmospheres. Thus 24 per cent of cold-pressed oil were obtained. The cold-pressed cakes were then broken up, comminuted, warmed to 150° F., and again expressed in the hot press at a pressure of 150 atmospheres. Thus a further quantity of hot-pressed oil, amounting to 22·7 per cent of the kernels, was obtained. The total amount of oil recovered from the kernels amounted to 46·7 per cent, as against the total contents of 57·26 per cent obtained by extraction with ether.

The oil extracted with ether—the total oil—had the iodine value 75·09.

The cold-pressed and hot-pressed oils were examined separately, and gave the following characteristics [3]:—

[1] *Chem. Zeit.* 1909, 76.

[2] *Seifensieder Zeit.* 1908, 1281.

[3] Lewkowitsch, *Analyst*, 1909, 10.

	Cold Pressed.	Hot Pressed.
Specific gravity at 40° C. (water at 40 = 1)	0·9179	0·9174
Specific gravity at 15° C. (water at 15·5 = 1)	0·9272	0·9327
Solidifying point	12° C.	14° C.
Melting point	15-36° C.	15-48° C.
Saponification value	197·1	196·4
Iodine value	75·67	71·25
Reichert-Meissl value	3·53	3·14
Unsaponifiable matter	1·51 per cent	2·04 per cent

Insoluble Fatty Acids

Fatty acids + unsaponifiable	95·15 per cent	92·66 per cent
Solidifying point (titer test)	35·45° C.	36·15° C.
Neutralisation value	192·4	192·0
Mean molecular weight of the fatty acids	291·5	292·1

The insoluble fatty acids consisted of :—

"Liquid" acids (yielding ether-soluble lead salts)	65·9 per cent	63·46 per cent
"Solid" acids (yielding ether-insoluble lead salts)	34·1 per cent	36·54 per cent
Iodine value of liquid fatty acids	107·4	108·0
Iodine value of solid fatty acids	16·56	17·87
Stearic acid	13·09 per cent	11·24 per cent

In contradistinction to the oil from *Carapa grandiflora*, the present oil does not contain any optically active substance.[1] The oil and the cakes have a very bitter taste, like all the corresponding products of the other Carapa species.

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Further specimens of Niam fat [2] furnished the following characteristics :

Oil—				
Specific gravity at 40° C.	0·9044	0·9044	0·9019	0·9016
Saponification value	181·5	194·6	180·7	183·3
Iodine value	69·8	70·3	72·1	72·5
Reichert-Meissl value	0·9	0·9	0·8	0·8
Unsaponifiable matter	0·5	...	...	0·86
Fatty Acids—				
Titer test, ° C.	49·0	47·0	47·5	48·5
Acid value	25·9	33·2	47·5	48

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PAYENA OIL, KANSIVE OIL

This oil is obtained from the seeds of *Payena oleifera*, a tree known in Burma as "kansive," and belonging to the natural family of *Bassia*. The following characteristics were ascertained by *D. Hooper* [3] :—

[1] The observations were made by *Dr. Pickles* in the Imperial Institute.
[2] *Bull. Imp. Institute*, 1908, 244. [3] Private communication to the author.

Fat—	
Specific gravity at 30° C.	0·915
Saponification value	198·9
Iodine value	63·4
Fatty Acids—	
Insoluble acids + unsaponifiable	94·5 per cent.
Melting point	38° C.
Acid value	26·2

The insoluble fatty acids yielded 35 per cent of ether-insoluble lead salts; the melting point of the fatty acids liberated from these salts was 55° C.

Kansive oil is used by the inhabitants of Burma for various purposes.

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Further investigations carried out by *J. Anderson*, Director of Botanical Gardens, Aburi, Gold Coast, in conjunction with *Evans*, show that there occur the following nine well-marked forms, differing in their botanical character, and also in their yield of oil (cp. for further details p. 442):—

Abe-tuntum fruits, medium size, reddish-black in colour; yield 13·7 per cent of oil.

Abe-pa fruits, large; colour, red streaked with black; yield 11·2 per cent of oil.

Abe-dam fruits, medium, red in colour with a tinge of yellow; yield 11·2 per cent of oil.

Abobo-be fruits, medium; colour, reddish-black. The shell of the kernel of this variety is so soft that it can be easily broken with the teeth; yield 19·3 per cent of oil.

Abe-fita ("white palm nut") fruits, large; colour, white streaked with black. The oil obtained from this variety is yellow in colour, and quite distinct from other commercial palm oils; yield 15 per cent of oil.

Abubu-be. This variety resembles *Abobo-be* in appearance, and the shell of the kernel is also soft, but the pericarp is much more fleshy, and the yield is greater, viz. 25 per cent of oil.

Adi-be fruits, large; colour, brick-red. This variety has a very fleshy pericarp, and the yield obtained is 28 per cent of oil.

Abe-ohene ("king of palms"). This variety has a medium-sized fruit, bright-red in colour, streaked with black; yield 15 per cent of oil.

It would appear from the above that *Abobo-be*, *Abubu-be*, and *Adi-be* are the best varieties to cultivate, but at the present time the natives of the Gold Coast do not appear to plant any particular variety.

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The examination of a genuine nutmeg butter, obtained by expressing genuine Ceylon nutmegs, was recently undertaken by *Power and Salway.*[1] The crushed nutmegs were subjected to a pressure of 4000 lbs. per square inch, at a temperature ranging between 45° and 75° C. for eight hours, and were allowed to remain under pressure for about twelve hours, during which time the temperature gradually fell. The yield amounted to 26·6 per cent.

[1] *Journ. Chem. Soc.* 1908, 1653.

The same raw material yielded on extraction with ether 42·9 per cent of fat.

The expressed fat represented, at the ordinary temperature, a soft brownish-yellow solid, having the characteristic odour of nutmeg.

The following table contains some characteristics of (1) the expressed fat, (2) the fat extracted by ether, (3) the expressed fat freed from essential oil by a current of steam, and (4) the total fatty acids :—

	Expressed Fat.	Fat extracted by Ether.	Expressed Fat free from Essential Oil.	Total Fatty Acids.
Melting point . .	48° C.	50° C.	49° C.	49° C.
Spec. grav. 50/50 C. .	0·9399	0·9337	0·9443	0·9012
Acid value . .	11·2	12·9	14·0	218·3
Saponification value .	174·6	180·5	199·6	...
Iodine value . .	57·8	45·7	35·7	23·1

The results of the investigation are summarised in the following table :—

Essential oil	12·5 per cent.
Trimyristin	73·0 ,,
Oleic acid, as glyceride . . .	3·0 ,,
Linolenic acid, as glyceride . .	0·5 ,,
Formic, acetic, and cerotic acids (very small amounts)	
Unsaponifiable matter . . .	8·5 ,,
Resinous material . . .	2·0 ,,
	99·5 per cent.

The unsaponifiable matter consisted of a substance of the formula $C_{18}H_{22}O_5$ (amounting to about 5 per cent of the expressed oil) and some myristicin, $C_{11}H_{12}O_3$,[1] and a very small amount of an alcohol, $C_{20}H_{34}O$, melting at 134°-135° C. This alcohol is described as a "phytosterol"; it differs from the ordinary phytosterol (sitosterol) (Vol. I. Chap. III.) by its different chemical composition, although it has the same melting point.

In addition to the *Myristica* species enumerated (pp. 459-69) the following other members of the "Myristica Group" are described by *D. Hooper*[2] :— *Myristica malabarica*, *M. canarica*, *M. guatemalensis*, *M. laurifolia*.

FAT FROM MYRISTICA MALABARICA

The seeds of *M. malabarica*, a tall evergreen tree growing in the forests of Konkan, Kanara, Malabar, and Travancore, are sold in Bombay as "kaiphal." The seeds contain 32 per cent of shells, and yield 40·76 per cent of fat and resins. The mace of the Bombay seeds differs entirely from that of the genuine mace from the official nutmeg. The mace of *M. malabarica* yields 63·26 per cent of fats and resins. The fat from the kernels of this species differs completely from the fat from *M. officinalis*. The characteristics of a Bombay fat (from *M. malabarica*) are given on p. 461, in the table due to *Spaeth*, and it will be observed that they differ entirely from those of the fat from *Myristica officinalis*.

[1] Power and Salway, *Journ. Chem. Soc.* 1907, 2037.
[2] *Agricultural Ledger*, 1907, No. 3.

FAT FROM MYRISTICA CANARICA

The seeds from *Myristica canarica* have been occasionally imported into this country under the name "Oil Nuts" from Africa and South America. In India the seeds are derived from the "Candle-nut tree," growing on the Western Ghats, from the Konkan southwards.

The entire seeds yield 49·4 per cent of fat; the mace, 54·6 per cent of fat; the kernels separated from the shells furnish 64·76 per cent of fat. The fat was light brown and crystalline, and gave in the cold with strong sulphuric acid a carmine-red colour.

The following characteristics were ascertained by *Hooper*:—

Fat—	
Melting point	37·5° C.
Saponification value	215·02
Iodine value	26·64
Fatty Acids—	
Insoluble acids + unsaponifiable	92 per cent.
Melting point	41° C.
Neutralisation value	217·53
Acid value	37·08

The solid fatty acid was separated by means of the lead-salt-ether method and was found to consist of myristic acid; the proportion of myristic acid was found to be 70·8 per cent.

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A combined hydraulic- and filter-press for the separation of cacao butter is patented by *M. A. Smith*, French patent 388,077.

PAGE 484

The Chinese tallow tree thrives well in the United Provinces of India and the Panjaub (Punjaub).[1]

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It should be pointed out that considerable confusion obtains in commerce with regard to the correct names of the "Pontianak," "Sarawak," and "Siak" fruits, which are imported and sold as "Illipé nuts" from Sarawak and Pontianak ("grosses graines de Pontianak et Sarawak") and from Siak ("petites graines de Siak"). The former are the fruits of *Shorea stenoptera* and the latter the fruits from a *Palaquium* species (*Dichopsis*). (The footnote 2 of page 492 should be deleted.)

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ARECA NUT FAT

This fat was obtained from the nuts of *Areca catechu*, L., by extraction. The colour as also the composition of the fat varies with the solvent used, as is evidenced by the data given in the following table:—

[1] Cp. D. Hooper, *Agricultural Ledger*, 1904, No. 2.

	Fat extracted with Ether.	Fat extracted with Petroleum Ether.
Fat—		
Colour	reddish-brown	yellowish-white
Odour	like nutmeg	nearly odourless
Specific gravity	0·884	0·973
Melting point	36°-37° C.	37°-38° C.
Saponification value	227·4	234·6
Iodine value	24·3	12·3
Reichert-Meissl value	0·2	4·2
True acetyl value	11·2	9·81
Unsaponifiable matter	1·12 per cent	1·01 per cent
Fatty Acids—		
Fatty acids + unsaponifiable	92·76 per cent	91·45 per cent
Melting point	39° C.	39°-40° C.
Mean molecular weight	244·6	238·5
Iodine value	25·95	13·6
Acid value	91·1	97·2

According to *Rathje*,[1] the fatty acids obtained from the two fats have the following compositions :—

	Fat extracted with Ether.	Fat extracted with Petroleum Ether.
	Per cent.	Per cent.
Stearic acid	2·25	3·3
Palmitic acid	3·1	2·5
Myristic acid	21·0	24·7
Lauric acid	43·7	53·3
Capric acid	1·0	1·0
Caprylic acid	...	small quantity
Caproic acid	...	small quantity
Oleic acid	29·0 (?)	14·5

In the author's opinion the fat extracted with petroleum ether would correspond best in its composition with the other fats belonging to the "Cocoa Nut Oil Group."

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According to the *Cocoa Nut Planters' Manual*, the area under cultivation for cocoa nut palms in 1907 was as follows :—

	Hectares.	Acres.
Ceylon	330,525	750,000
South America	202,350	500,000
India	161,880	400,000
Straits Settlement, Philippines	141,645	350,000
Java, Sumatra	101,175	250,000
South Sea (Pacific Islands)	105,200	260,000
Mauritius, Seychelles, Madagascar, Zanzibar, Réunion, and East African Coast	44,517	110,000
Siam and Cochin China	40,470	100,000
West Indies	44,517	110,000

[1] *Archiv der Pharm.* 1908, 702.

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KHAKAN (KAKAN) FAT, KILNEL OIL

This fat is obtained from the seeds ("pilu or jhal") of *Salvadora oleoïdes*, Dene. (*S. indica*, Royle), a small tree or shrub growing in Northern India. The seeds contain 45·48 per cent of fat. The following characteristics were ascertained by *Hooper*.[1] The low iodine value in conjunction with the high saponification value induce the author to place this fat amongst the fats of the Dika group.

Oil—	
Specific gravity at 50° C.	0·9084
Melting point	41° C.
Saponification value	242·36
Iodine value	7·48
Reichert-Meissl value	1·28
Fatty Acids—	
Insoluble fatty acids	94·12 per cent.
Melting point	40° C.
Neutralisation value	244·42
Iodine value	8·3
Acid value	11·26

The fat is employed in Cutch in the manufacture of "bangalas" (outer garments of Cutchee ladies).

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By converting the glycerides into methylesters, and fractionating the latter at a pressure of 25 mm., *Bontoux* ascertained that caÿ-caÿ fat consists of about 5 per cent of olein, 30-35 per cent of laurin, and 65-60 per cent of myristin (*Les Matières Grasses*, 1908, 1277).

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The following characteristics have been ascertained for specimens of lard stearine by *Arragon*[2]:—

	I.	II.	III.	IV.	V.
Specific gravity at 100° C.	0·8585	0·8580	0·8575	0·8578	0·8588
Saponification value	...	195·5	195·5	195·5	194·5
Iodine value	50·7	50·9	48·9	49·6	54·3
Butyro-refractometer "degrees" at 40° C.	48·5	48·3	47·7	47·5	48·7
Crystals, exhibiting the form of	plates	plates	plates	plates	plates

[1] *Agricult. Ledger*, 1908, No. 1.

[2] *Chem. Zeit.* 1908, 1227.

PAGE 632

The quantity of tallow exported from the United States in 1907 was 127,857,739 lbs. The export of tallow in the (fiscal) year 1908 was 91,397,507 lbs. of the value 5,399,219 dollars. The amount of tallow imported into the United States is given in the following table :—

Fiscal Years.	Lbs.	Value in Dollars.
1904	104,767	11,662
1905	278,188	16,887
1906	908,259	63,805
1907	424,876	29,925
1908	304,765	23,074
	2,020,855	145,353

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With regard to the keeping properties of butter in cold storage cp. *W. S. Sayer*, *O. Rahn*, and *Bell Ferrand*.[1] With regard to the influence of salt on the micro-organisms (bacteria, fungi) occurring in butter, and on the *optimum* percentage of salt, cp. *O. Fettick*.[2]

PAGE 736

Bougault and Bourdier[3] describe a new class of vegetable waxes obtained from the leaves of coniferous plants (*Juniperus Sabina*, *J. communis*, *Picea excelsa*, *Pinus sylvestris*, *Thuja occidentalis*) by boiling out with 90 per cent alcohol. These waxes differ in their chemical constitution from all other waxes described in this work, in that they do not yield an alcoholic constituent like cetyl- or melissyl-alcohol on saponification, both constituents of the waxes obtained by saponification having an acid character. Hence, if barium chloride solution be added to the alcoholic solution obtained on saponifying the waxes with alcoholic potash, and the dried precipitate be treated with petroleum ether or cold ether, nothing is thereby extracted. These waxes are therefore judged to be the esters of acids containing an alcoholic hydroxyl (alcoholiform) group, and the esters seem to have been produced by the radicle of the acidic constituent entering into chemical combination (esterification) with another molecule of the same or a similarly constituted alcoholiform acid. The authors therefore propose for these substances the name *etholides*, and compare them in their constitution with *Fischer's* peptides, which are formed from aminoacids. (In the author's opinion it would appear more appropriate to compare these products with the polyricinoleic acids, which ricinoleic acid is capable of forming.)

[1] *Zentralbl. f. Bakterien u. Parasitenkund.* ii. 22 (1908), 22.
[2] *Ibid.* ii. 22 (1908), 32. [3] *Compt. rend.* 1908, 147, 1311.

The wax obtained from *Juniper Sabina* melts from 73° to 78° C., and can be resolved by treatment with solvents into fractions melting at 68°, 72°, 76°, and 82° C. respectively.

The acid value of the constituents into which the waxes are resolved by saponification varied from 25 to 54; the saponification value was about 230. As they are able to absorb acetyl groups in the acetylation test it is concluded by the authors that the constituents contain alcoholic hydroxyl groups. Hitherto two hydroxy acids have been isolated, viz. a hydroxylauric acid, $C_{12}H_{24}O_3$, melting at 84° C. (which the authors propose to term *sabinic* acid), and a hydroxypalmitic acid, $C_{16}H_{32}O_3$ (which the authors propose to term *juniperic* acid).

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